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### REFERENCE


Lane, B. H., 1935, Suggestions to authors of papers submitted for publication by the United States Geological Survey: U. S. Geol. Survey, Washington, D. C. (For sale by Superintendent of Documents, Washington, D. C. 35c.)

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*SEPTEMBER 1955*

# THERMOMETRIC AND PETROGENETIC SIGNIFICANCE OF TITANIFEROUS MAGNETITE*

A. F. BUDDINGTON, JOSEPH FAHEY, and ANGELINA VLISIDIS

ABSTRACT. This study of the variation of the titanium content of magnetite relative to its host rock utilized over 200 analyses, about half of which are from the literature and the other half contributed by the authors. The percent of $TiO_2$ in magnetite varies widely. Correlation of data leads to the conclusion that in the $Fe_3O_4$—$FeO.TiO_2$ system, where ilmenite is present in excess as independent grains, the percent of $TiO_2$ in magnetite is largely a function of temperature. The composition of the system in which the titaniferous magnetite formed may be a modifying factor. This is especially significant where the alternative development of $2FeO.TiO_2$ instead of $FeO.TiO_2$ occurs. The potentialities of using the composition of titaniferous magnetite for relative geological thermometry are set forth. The data serve to re-emphasize that the formation of granophyre, microperthite granite, and most titaniferous magnetite-ilmenite deposits are at *magmatic* temperatures; also, that accessory titaniferous magnetite develops contemporaneously with the silicate minerals of granites instead of at a late stage only.

## INTRODUCTION AND ACKNOWLEDGMENTS

The present work is a by-product of a study initiated by James Balsley and A. F. Buddington on the correlation of magnetic anomalies of the northwest Adirondacks area in New York with mineralogy and geology. This study, which has been in progress for a period of about six years, was made under the auspices of the U. S. Geological Survey. Balsley has been responsible for the geophysical aspects of the problem, Buddington for the mineralogy; Fahey and Vlisidis have had responsibility for the analytical chemical work. The complete report on the mineralogy of the iron and titanium oxides and their correlation with the geology and magnetic data will be submitted later for publication by the U. S. Geological Survey.

We are deeply indebted to the following geologists: to Rodney Bleifuss for generously contributing for our use his unpublished data in connection with a master's thesis at the University of Minnesota on the percent of $TiO_2$ in titaniferous magnetites of many Minnesota rocks; to E. A. Vincent of Oxford University, England, for courteously lending us before publication a copy of his manuscript on the Skaergaard titaniferous magnetites; to Hisashi Kuno who first called our attention to the work by Iwasaki and Katsura on the composition of titaniferous magnetites in Japanese lavas; to T. Broderick, Michael Fleischer, Gordon Macdonald, and J. A. Noble who furnished us pertinent information, and to Freleigh Osborne and A. W. Postel who each secured a rock sample for us.

## SAMPLING AND POSSIBILITIES FOR ERROR

The samples of the Adirondack rocks in all cases except where the field number is succeeded by an S (as in 51-S) are grab samples to the amount

* Publication authorized by the Director, U. S. Geological Survey.

of 10 or 20 pounds collected as chips from outcrops along traverses a thousand feet to two miles in length. Samples with a number followed by S are single pieces.

The samples for analysis were prepared by crushing and sieving so as to obtain a fraction between 80 and 270 mesh. The titaniferous magnetite was then separated with a hand magnet and analyzed. For the purpose of the original study it was not deemed necessary to obtain pure concentrates. About 15 percent of the analyzed magnetic concentrates ran between 80 and 85 percent, and 15 percent ran between 85 and 90 percent total $FeO+Fe_2O_3+TiO_2$, about 30 percent of the concentrates were between 90 and 95 percent, and about 40 percent were more than 95 percent total $FeO+Fe_2O_3+TiO_2$. The contaminants were largely quartz and feldspar, which would be effectively neutral so far as affecting the analyses for iron and titanium. To a slight extent, such mafic minerals as pyroxene, hornblende, garnet, and ilmenite were present either separately or as compound grains with the titaniferous magnetite. These would introduce a slight but insignificant error in the analytical results.

Polished surfaces and thin sections of each rock from which the titaniferous magnetite was concentrated have been studied to determine the nature of the iron and titanium oxides, the degree and nature of metamorphism and recrystallization, and any deuteric and secondary alterations present. The latter is especially important where secondary magnetite from alteration of mafic minerals might act as a contaminant.

The data are subject to several sources of error in addition to the silicate contaminants previously mentioned. In some grains, ilmenite forms exsolved blades on the borders of the magnetite grains and may in part be ground off and lost in the crushing. Some primary grains are compound and consist of titaniferous magnetite and independent ilmenite grains. A few of these tend to be among the contaminants.

The fineness of grinding and strength of the magnetic field used in concentrating the magnetite may also affect the composition of the concentrate.

## FACTORS IN INTERPRETATION

There are many possibilities for error in the proper interpretation of the significance of the $TiO_2$ content of the magnetite. Major ones are the selection of the correct hypothesis for the origin of the intergrowths, the degree of variation of $TiO_2$ dependent upon the polycomponent nature of titaniferous magnetite, the proper explanation for the inhomogeneity of the magnetite from grain to grain in some host rocks, a correct understanding of the variation in the composition of the titaniferous magnetite with the composition of the system in which it forms, and the degree of equilibrium attained for a restricted temperature range.

*Titaniferous magnetite a polycomponent system.*—It is known experimentally (Pouillard, 1950) that FeO, $Fe_2O_3$, and $TiO_2$ form a polycomponent system at high temperatures with the development of the compounds magnetite ($FeO.Fe_2O_3$), ilmenite ($FeO.TiO_2$), ulvöspinel ($2FeO.TiO_2$), and a tetragonal titanate ($2Fe_2O_3.3TiO_2$) with more or less solid solution among them.

The term *titaniferous magnetite* is used herein as a general one to include all titanium-bearing magnetites. The following varieties are among those included; titanmagnetite (a single-phase solid solution of $TiO_2$ compounds in magnetite); ilmenomagnetite (a microintergrowth of ilmenite in magnetite); and mogensenite (a microintergrowth of ulvöspinel in magnetite). The ilmenite intergrowth in the magnetite may occur as a very fine film to a thin platelike grid oriented parallel to the *octahedral* planes of the magnetite, as coarse blades parallel to a single plane, or as actual granules in or on the borders of the magnetite grains depending on the amount and degree of migration of the exsolved material. All are considered the product of exsolution of an originally homogeneous mineral.

The intergrowth of ulvöspinel in magnetite is usually very fine and not visible below a magnification of several hundred diameters. The exsolved material is normally oriented on the *cubic* planes of the magnetite (Ramdohr, 1953).

Ferrous iron in excess of that necessary to form magnetite and ilmenite occurs in many magnetites from gabbroic and volcanic rocks. Foslie (1928) assumed that $2FeO.TiO_2$ *ordinarily* forms and enters into solution in the magnetite in the crystallization of highly ferriferous titanium-bearing magmas if an excess of $Fe_2O_3$ is not present. Mogensen (1946) confirmed the presence of ferrous orthotitanate as a major constituent of magnetite concentrations at Södra Ulvön, and Ramdohr (1953) has shown that ulvöspinel occurs as exsolved intergrowths in the magnetites of many ilmenite-magnetite segregations of gabbroic rocks. Vincent and Phillips (1954) found it in some of the magnetites of the Skaergaard complex, and Girault (1953) has also described it. Exsolved ilmenite intergrowths also occur with the exsolved ulvöspinel in many of the magnetites, or its presence is indicated by recomputation of chemical analyses. Ferrous iron in excess of that required to form ferrous orthotitanate has also been found in many magnetites. Recomputation of chemical analyses and the size of the unit cell are consistent with the presence of the compound $2FeO.TiO_2$ together with excess FeO in analyzed magnetite of several green pyroxene granite gneisses and in granulite formed by reconstitution of olivine diabase in the Adirondacks. Ilmenite is also present.

Excess $Fe_2O_3$, instead of FeO, over that necessary to form ilmenite occurs in all the magnetite of the Adirondack granitic rocks, except some of the green pyroxene granite. The available chemical analyses of magnetite from rhyolite and some dacite may also be recomputed in terms of ilmenite alone or ilmenite with a little excess $Fe_2O_3$. Most basalts and olivine-rich gabbros appear to have a magnetite with $2FeO.TiO_2$ with or without excess FeO as a major component in solution, but some tholeitic basalt, some olivine gabbro and pyroxene gabbro, and some diabase have magnetite with $FeO.TiO_2$, with or without excess $Fe_2O_3$ in solution.

Experimentally (Greig, Posnjak, Merwin, and Sosman, 1935) found that at 1075°C. a magnetite with 8 ($\pm$ 1) percent $Fe_2O_3$ in solid solution can coexist in equilibrium with hematite. Analyses of the ilmenomagnetite in the Adirondack hornblende microperthite granite have consistently shown from

8 to 10 percent excess $Fe_2O_3$. Neither X-ray nor microscopic examination of polished surfaces has shown hematite as a separate mineral in any of these ferric titaniferous magnetite samples. The $Fe_2O_3$ may be calculated as $Fe_2O_3$, as $2Fe_2O_3.3TiO_2$, or as $Fe_2O_3.TiO_2$ in solid solution. In the last-named formula the amount calculated as ilmenite will be decreased and magnetite increased.

Under appropriate physicochemical conditions MgO may substitute for FeO in the magnetite instead of occurring in the silicates. We have, however, found magnesioferrite only as a *very* minor component of the Adirondack magnetites.

Small amounts of other elements such as aluminum (in part in exsolved spinel), vanadium, calcium, and manganese may also enter into the magnetite structure, and still other elements may be present in smaller amounts or in traces.

The ilmenite in association with ilmenomagnetite of rocks ranging from gabbro to granite is also of variable composition. It may therefore be expected that there will be a *range* for the percent of $TiO_2$ in magnetite for any given temperature depending upon the chemical composition of the system.

*Interpretation of intergrowths in magnetite.*—Three major possible interpretations for the origin of the ilmenite and ulvöspinel intergrowths in the magnetite are replacement, contemporaneous crystallization, or exsolution. No veinlike or other fabric patterns have been found to suggest that the intergrowths are in any part due to replacement in any of the rocks for which we are using data. The systematic correlation and narrow range of composition of the magnetite with the nature of its different host rocks are definitely contrary to the concept of origin by replacement.

Ilmenomagnetite and ilmenite occur as separate independent grains. We have found no intergrowth of these two minerals, which seem best interpreted in terms of simultaneous primary crystallization.

In the plutonic rocks, the titanium compounds in magnetite normally occur as microintergrowths, whereas in quickly chilled volcanic rocks of equivalent composition they may occur in corresponding amounts in solid solution in the magnetite. This is consistent with the hypothesis of origin of the microintergrowths by exsolution.

It is therefore assumed here that the intergrowths of ilmenite and ulvöspinel in magnetite are of exsolution origin. The succeeding data will show that making such an assumption permits the development of an hypothesis to explain the variation of the $TiO_2$ content of magnetite which is consistent with much other data.

In some examples it can be inferred that the bulk *composition* of the rock is not the factor in controlling the composition of the titaniferous magnetite. In the case of metamorphic reconstitution at successively lower temperatures, the total composition remains constant while the composition of the titaniferous magnetite changes. The titaniferous magnetite of the Adirondack pyroxene granites generally carries 8-10 percent $TiO_2$, whereas the titaniferous magnetite of the equivalent gneisses formed from them under the physical conditions of the granulite or higher portion of the temperature range of the amphibolite facies have only 3.5-4.0 percent $TiO_2$. Similarly, the titaniferous

magnetite of the microperthite alaskite and hornblende microperthite granite has in general 3.6-6.7 percent $TiO_2$, whereas that of the equivalent gneisses formed in the higher portion of the temperature range for the amphibolite facies has 3-3.5 percent $TiO_2$ and only 1-3 percent $TiO_2$ in the gneisses formed in the lower portion of the temperature range for the amphibolite facies.

*Inhomogeneity and inequilibria.*—There is good evidence that in many cases the titaniferous magnetite in a rock is inhomogeneous from one grain to another or even within a single grain. The titaniferous magnetite may *not* be an equilibrium assemblage for any one temperature. The bulk of the titaniferous magnetite *may* represent a mineral formed through a very narrow temperature range, but commonly there will be some formed at lower temperatures than the bulk and some formed at higher temperatures.

Furthermore, deuteric and late-stage alterations and recrystallizations at relatively low temperatures may affect part of the titaniferous magnetite formed at higher temperatures. This is clearly demonstrated by the local development of sphene coronas around magnetite, the partial replacement by hematite, or—at an extreme—the complete recrystallization of an original intergrowth into separate grains. The partial chloritization of part of the mafic minerals at relatively moderate temperatures may result in the formation of a $TiO_2$-poor secondary magnetite that might concentrate with any unaltered titaniferous magnetite and serve to dilute it.

Or again, *new* relatively pure magnetite may be introduced at a different period by hydrothermal solutions without necessarily a complete reworking of the older primary titaniferous magnetite of the rock.

The exsolution and migration of the ilmenite from the magnetite of plutonic igneous rocks may go so far that the primary titaniferous magnetite is effectively recrystallized by deuteric solutions to a granular aggregate of magnetite and ilmenite. When this happens the composition of the magnetite would obviously give the temperature of recrystallization and not the temperature of primary formation.

A thorough study of the geology of the surrounding rocks and of the silicate minerals accompanying the oxides must always be made in order to check on the possible modifications which the rock may have undergone.

The degree of unmixing and separateness of the alkali feldspars, where they occur, as in granites and equivalent gneisses, is of very great help. The solvus for $K_2O.Al_2O_3.6SiO_2$ and $Na_2O.Al_2O_3.6SiO_2$ has been determined between 500° C. and the temperature of complete solid solution (660° C.) by Bowen and Tuttle (1951). The degree to which two separate alkali feldspars are present—either as intergrowths or as separate grains—together with their nature and degree of heterogeneity may give substantial evidence on the extent to which an equilibrium assemblage is present and under what conditions it formed. Similarly in the mafic igneous rocks and gneisses the nature of the pyroxenes may afford clues. The presence of chlorite, sericite, and other hydrothermal silicates may also help to throw light on the story of the oxides.

### PROBABLE TEMPERATURE OF FORMATION OF VARIOUS HOST ROCKS

We are interested in the manner in which the composition of titaniferous magnetite varies with the temperature. It is therefore pertinent to inquire into

the probable range of temperature at which the rocks containing the analyzed magnetite were formed.

Gordon A. Macdonald (1953, written communication) states that the extrusion temperatures of basaltic lava flows at Hawaii are generally between 1000° and 1100° C., and that the final temperature of immobilization of aa flows is probably between 700° and 780° C., though no doubt some groundmass crystallization occurs before final immobilization. The temperature of Hawaiian lava may reach 1200° C. The andesitic basalt lava at Parícutin also had a temperature of 1200° C. (Foshag, 1950, p. 752). A sample of the Palisades (New Jersey) diabase heated at atmospheric pressure was not half molten until about 1225° C. (Sosman and Merwin, 1913) but failed to initiate melting in an inclusion of arkose which itself was half molten at 1150° C., indicating that its intrusion temperature was less than this. Pigeonite occurs as an essential mineral in many diabases, and this has been inferred by Hess (1941, p. 582-583) to indicate that the temperature was above the inversion interval for the orthorhombic pyroxenes, probably above 1000° C. and perhaps around 1100° C.

Wager and Deer (1939, p. 111) find that in certain layers of the Skaergaard gabbro mass a pyroxene of the hedenbergite-ferrosilite solid-solution series is probably the result of inversion from an iron-rich $\beta$-wollastonite solid solution. This would necessitate a crystallization temperature above 940° C. Wager and Deer (quoted in Wager, Weedon, and Vincent, 1953) found what is interpreted as quartz inverted from tridymite in the groundmass of ferrogabbro. If this is an equilibrium phenomenon it would necessitate a temperature of greater than 870° C. for the crystallization of the groundmass.

In basaltic magma, magnetite commonly does not separate until after a substantial portion of the magma has crystallized. It may therefore be expected to form in *basaltic* lavas generally below 1100°, commonly perhaps around 1000° C., and may with undercooling extend as low as 800° C.

Kuno (Kuno and Nagashima, 1952, p. 1005) on the basis of the occurrence of microphenocrysts of hypersthene and pigeonite and their inversion interval has estimated the temperature of *basaltic andesite* at time of extrusion as 1100° C.

The temperature of *augite hypersthene andesite* lava at the time of extrusion at Semetu in Java has been recorded as between 960° and 1060° C.

The temperatures of extruded dacitic lava at Santorini have been reported (Georgalas and Papastamatiou, 1953, p. 24) as in general between 800° C. and 920° C. with a maximum of 975° C. Kenzo Yagi (1953) reports hypersthene dacitic lava (69.7 percent $SiO_2$) with magnetite phenocrysts to have commonly shown temperatures of 800°-900° C. in the crevices of the molten lava. The extremely viscous lava extruded at Santiaguito in Guatemala was found by Zies (1941) to be at a temperature of 700°-725° C. and 750° C. (1951). Phenocrystic magnetite of *dacitic* lavas therefore probably formed in general between 900° and 750° C.

Some experimental data have a bearing on probable temperatures of granitic and rhyolitic magma. Bowen and Tuttle (1950) have shown experimentally that the temperature for complete solubility of $NaAlSi_3O_8$ and

$KAlSi_3O_2$ in the ratios to each other comparable to that found in the alaskite of the Adirondacks is 660° C. The plagioclase of the alaskite, however, is an oligoclase instead of albite, so that assuming the potash and soda-lime feldspars originally crystallized as sanidine the temperature would have had to be above 660° C.

Bowen and Tuttle (1951) also find that the minimum melting temperatures for mixtures of $NaAlSi_3O_8$, $KAlSi_3O_8$, and $SiO_2$ under water vapor pressures of 2000 kg/cm² and 3000 kg/cm² are respectively 675° and 670° C. The addition of $CaAl_2Si_2O_8$ or a lower vapor pressure would tend to raise this temperature. The presence of hyperfusible compounds would tend to lower it. In general the temperature of *granitic* and rhyolitic magmas may be inferred to be between 675° C. and 850° C. and for much of it between 700° and 800° C. The temperature of injected simple *granite pegmatite* may be expected to be lower than this, perhaps around 550°-700° C.

The terms *microperthite* and *microantiperthite* as used here refer exclusively to feldspars with intergrowths of potash feldspar and plagioclase with normative $KAlSi_3O_8$ forming 38 to 55 percent of the total feldspar.

The rocks of the garnetiferous granulite facies carry two feldspars as separate grains; the potash feldspar is moderately strongly microperthitic but not as much so as in the alaskite. The metamorphic reconstitution of these garnetiferous rocks must have gone on below, but only very slightly below 660° C. The ilmenomagnetite of these rocks carries in general about 3.7 percent $TiO_2$, which appropriately is less than that of the alaskite. The $TiO_2$ content of the magnetite is in part the same in the alaskite as in the granulites. The alaskite is thought to have crystallized at temperatures slightly above the temperature of formation of the rocks of the granulite facies and its similar percent of $TiO_2$ in magnetite may be due to a slight modification of the primary ilmenomagnetite of the alaskite by deuteric solutions of slightly lower temperature. Rosenqvist (1952) estimates the temperature range for metamorphism in the granulite facies as 500°-900° C. for depths of about 11 and 6 miles respectively. The Adirondack granulite rocks were at depths greater than 5 miles at the time of reconstitution. Their temperature range of formation may be estimated as between 500° C. and 700° C.

Smith (1953, p. 451) determined the decrepitation temperature of the pyralmandite and hornblende from garnet amphibolite at the Barton mine, New York, as 613° ± 30° and 603° ± 20° C. respectively. He suggests the possibility that the rock was formed around these temperatures corrected for the effect of pressure during recrystallization. The amphibolite occurs in an area where the rocks belong to the granulite facies and is thought to belong to this facies (Buddington, 1952, p. 83).

Ramberg (1952, p. 137) estimates the temperatures for the amphibolite facies as between 350°-550°C. Rosenqvist (1952, p. 101) suggests a temperature range of 400°-750° for the amphibolite facies at all depths less than 8 miles.

TABLE 1

Chemical Composition of Titaniferous Magnetite in Volcanic Rocks, Japan

| Sample no.* | $SiO_2$ | $TiO_2$ in magnetite | $V_2O_5$ in magnetite | Magnetite recomputed to 100% | | | | | Estimate of temperature range** |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $Fe_3O_4$ | $2FeO.TiO_2$ | $FeO.TiO_2$ | FeO | $Fe_2O_3$ | |
| **Olivine basalt** | | | | | | | | | |
| T-4 N-14 | — | 18.37 | 1.13 | 53.3 | 36.9 | 9.8 | — | — | |
| N-3 | — | 20.10 | — | 55.1 | 20.8 | 24.0 | — | — | |
| T-3 | 47.38 | 21.05 | 0.36 | 58.1 | 6.0 | 35.9 | — | — | |
| **Tholeitic basalt** | | | | | | | | | |
| T-5 N-13 | 51.0 | 17.55 | 1.04 | 60.4 | — | 33.2 | — | 6.4 | |
| | | 19.98 | | | | | | | 20-14% $TiO_2$ 1200°-1000°C. |
| | | 18.02 | | | | | | | |
| | | 17.52 | | | | | | | |
| | | 17.49 | | | | | | | |
| | | 17.00 | | | | | | | |
| **Ground mass, pyroxene andesite, pigeonitic series** | | | | | | | | | |
| T-6 | 51.5 | 14.22 | 0.49 | 59.7 | 39.8 | — | 0.5 | — | |
| N-12 | — | 20.2 | — | 53.3 | 26.2 | 20.5 | — | — | |
| N-15 | | 15.8 | — | 51.7 | 44.1 | — | 4.1 | | |
| | | 16.82 | | | | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Phenocrysts in andesite** | | | | | | | | | |
| N-4 | — | 12.4 | | 71.5 | 15.2 | 13.2 | — | — | 14-10% $TiO_2$ 1100°-900°C. |
| N-6 | — | 9.0 | — | 63.7 | 25.1 | — | 9.2 | — | |
| N-7 | — | 13.8 | — | 62.5 | 35.6 | 2.0 | — | — | |
| N-10 | — | 12.3 | — | 66.7 | 30.9 | 2.4 | — | — | |
| T-9 | | 6.43 | 0.50 | | | | | | |
| **Phenocrysts in pyroxene dacite** | | | | | | | | | |
| N-8 | — | 12.0 | — | 44.0 | 33.6 | — | 22.4 | — | |
| N-5 | | 12.2 | — | 42.1 | 34.0 | — | 23.9 | — | |
| **Phenocrysts in hornblende dacite, in part pumice** | | | | | | | | | |
| N-2 | — | 13.7 | — | 52.3 | 38.3 | — | 9.4 | — | 10-7% $TiO_2$ 900°-800°C. |
| N-9 | — | 6.8 | — | — | — | — | — | — | |
| N-11, T-10 | 58.7 | 7.42 | 0.45 | 83.8 | 6.5 | 9.7 | — | — | |
| | — | 10.30 | — | | | | | | |
| T-9 | — | 9.54 | 0.44 | 82.0 | — | 18.0 | — | — | |
| **Dacite** | | | | | | | | | |
| T-7 | 58.7 | 11.24 | 0.63 | 76.4 | 6.9 | 16.6 | — | — | |
| T-12 | 67.7 | 11.25 | 0.36 | 78.7 | — | 21.3 | — | — | |
| **Phenocrysts in liparite** | | | | | | | | | |
| N-1 | 76.3 | 4.13 | 0.25 | 91.1 | — | 7.8 | — | 1.1 | 4 to < 4% $TiO_2$ 800°C.- |

* Numbers preceded by letter N are from Nagata (1953, p. 40), those preceded by letter T are from Taneda (1950, p. 417), analyses without numbers were furnished by Kuno (personal letter). All analyses are by Iwasaki, I., and Katsura, T. (1950) or by Katsura (Taneda, 1950). The original of the paper by Iwasaki and Katsura (1950, in Japanese) has not been seen by the authors.

** Estimate of temperature by Kuno (personal letter dated June 6, 1953) for formation of rock.

## DATA ON VARIATION IN COMPOSITION OF TITANIFEROUS MAGNETITE WITH VARIATION IN NATURE OF HOST ROCK

Data on the variation of $TiO_2$ in titaniferous magnetite of the Adirondack rocks and some pertinent analogous data from the literature are given in the accompanying tables. It will be noted that in general the percent of $TiO_2$ in the accessory magnetite of plutonic rocks is lower than in that of the volcanic rock of equivalent chemical composition. Quartz and alkali feldspars similarly have been found to have properties indicative of a higher temperature for the volcanic than for the plutonic equivalent (Bowen and Tuttle, 1950; Keith and Tuttle, 1952). Where $TiO_2$ in the magnetite of the plutonic rocks exceeds about one percent, ilmenite is present as an exsolved intergrowth.

TABLE 2

Variation in Percent of $TiO_2$ in Accessory Titaniferous Magnetite of Basalt, Diabase, and Granophyre in Minnesota*

| Granophyre (Red Rock) | | |
|---|---|---|
| | Percent magnetite | Percent $TiO_2$ in magnetite |
| Northland sill | 2.5 | 7.5 |
| Endion sill | 0.7 | 4.0 |
| Lake shore in Duluth, 50 feet E. of 22d Ave. E. | 1.0 | 4.4 |
| Lester River sill, 825 feet above base | 0.6 | 9.8 |

| Diabase | | Basalt | |
|---|---|---|---|
| Percent magnetite in rock | Percent $TiO_2$ in magnetite | Percent magnetite in rock | Percent $TiO_2$ in magnetite |
| 1.2 | 20.1 | 1.2 | 10.2 |
| 0.9 | 20.1 | 0.9 | 9.7 |
| 0.9 | 20.0 | 1.4 | 8.1 |
| 1.4 | 18.0 | 2.2 | 6.8 |
| 0.9 | 17.9 | 1.6 | 6.6 |
| 0.5 | 17.7 | 2.5 | 6.5 |
| 0.6 | 16.0 | 1.3 | 6.3 |
| 0.5—3.4** | 4.0—10.4** | 1.6 | 5.7 |
| | | 1.5 | 4.5 |
| | | 2.0 | 4.0 |
| | | 0.9—1.5† | 2.5—3.5† |

* Bleifuss, R. L., 1953, personal communication.

** Range of 8 analyses in addition to those listed above.

† Range of 4 analyses in addition to those listed above.

TABLE 3

Variation in Percent of $TiO_2$ in Accessory Titaniferous Magnetite of Gabbro in Minnesota (a)

| Percent magnetite in rock | Percent $TiO_2$ in magnetite |
|---|---|
| 0.5 | 11.1 |
| 0.3 | 10.5 |
| 0.4 | 10.6 |
| 0.3 | 9.7 |
| 0.8 | 9.5 |
| 0.4 | 9.1 |
| 0.2 | 8.9 |
| 0.3 | 8.4 |
| 0.2 | 7.5 |
| 0.7 | 7.5 |
| 0.3 | 6.8 |
| 0.3 | 4.4 |

(a) Bleifuss, R. L., 1953, personal communication.

TABLE 3-A

Variation of Percent $TiO_2$ in Magnetite of Magnetite-Ilmenite Segregations in Gabbro in Minnesota (b)

| | Percent Fe in magnetic concentrate | Percent $TiO_2$ in magnetic concentrate |
|---|---|---|
| c | 54-58 | 18.72-20.80 |
| d | 58 | 15 |

(b) Grout, F. F., 1949-1950.

(c) Segregation at Poplar Lake, magnetic concentrates with more than 54 percent Fe, Grout, p. 37-38.

(d) Magnetic concentrates from segregation with 20-36 percent heavy concentrates, Grout, p. 64.

TABLE 4

**Variation in Percent $TiO_2$ in Ilmenomagnetite or Magnetite of Adirondack Igneous Rocks, Gneisses, and Veins; Accessory unless Otherwise Noted**

| | Field no. | Percent $TiO_2$ |
|---|---|---|
| Hornblende microperthite granite. | 36 | 5.3 |
| | 38 | 6.05 |
| | 51-S | 5.04 |
| | 79 | 6.70 |
| | 100-S | 5.53 |
| | 110-b | 5.2 |
| Microperthite alaskite. | 37 | 4.3 |
| | 39 | 4.1 |
| | 64 | 3.1 |
| | 142-S | 3.6 |
| | 179 | 3.1 |
| | 191 | 3.1 |
| Transitional potash-rich microperthitic microcline alaskite. | 53 | 3.46 |
| | 108 | 3.14 |
| | 109 | 3.82 |
| Granite pegmatite. | 111 | 2.33 |
| Oxide-rich concentrations as part of granite pegmatite. | 165 | 2.62 |
| | L-2501 | 2.45 |
| Muscovite-microcline granite pegmatite. | 210-B | 0.51 |
| Hornblende granite gneiss, low range of amphibolite facies, microcline and plagioclase as separate grains. Sphene present. | 12 | 0.64 |
| | 15 | 1.08 |
| | 23-S | 2.30 |
| | 26 | 2.93 |
| | 99-A | 2.92 |
| | 99-AB | 1.75 |
| | 184 | 1.23 |
| | 186 | 2.11 |
| | 188 | 0.70 |
| | 189 | 1.58 |
| | 211 | 1.27 |
| Hornblende granite gneiss, higher range amphibolite facies. Microcline, trace to slight microperthitic intergrowth. | 3 | 3.45 |
| | 8 | 3.38 |
| | 59 | 3.09 |
| | 102 | 3.9 |
| | 197 | 3.65 |
| Pyroxene microperthite granite. | 192 | 9.6 |
| | 216 | 8.2 |
| Pyroxene syenite and quartz syenite gneiss, higher range amphibolite facies. Microcline trace to slight microperthitic intergrowth. | 67 | 3.68 |
| | 141 | 3.84 |
| | 193 | 3.15 |
| | 58-b | 4.21 |
| Microcline-rich granite gneiss by granitization. | 45 | 2.22 |
| | 56 | 3.08 |
| | 80 | 3.09 |
| | 86 | 2.64 |
| | 107 | 2.60 |
| | 127 | 2.71 |
| | 131-a | 3.15 |
| Vein concentrations magnetite-apatite-pyrite-ilmenite. | 176 | 3.9 |
| | 177 | 1.2 |
| | 180 | 4.3 |
| Replacement disseminations (5-6 percent) in gneiss. | NP-SA | 1.6 |
| | 74 | 1.5 |
| | 166 | 1.2 |
| Pyroxene microperthite alaskite, magnetite with sphene coronas. | 187 | 2.8 |
| | 178 | 2.2 |
| Biotite microperthite pegmatite seam in biotite microperthite granite. | 181 | 5.7 |
| Pyroxene and pyroxene hornblende granite gneiss, potash feldspar moderately microperthitic, garnetiferous granulite facies. | 2 | 5.1 |
| | 4 | 3.5 |
| | 5 | 2.6 |
| | 124 | 3.55 |
| Gabbro and anorthosite reconstituted in garnetiferous granulite facies. | 129 | 4.23 |
| | 157 | 3.27 |
| | 158 | 4.10 |
| | 161 | 3.80 |
| | 208-a | 3.0 |

TABLE 4-A

Composition of Magnetite in Rocks of Lake Sanford Area, N. Y.

| Sample no. | | Wt. percent magnetic concentrate | Percent $TiO_2$ | Percent $V_2O_5$ |
|---|---|---|---|---|
| | Rich ore, lens 2, Sanford Hill* | 78.6 | 12.09 | 0.58 |
| | Rich ore, lens 1, Sanford Hill* | 80.2 | 14.43 | 0.64 |
| 203 | Rich ore, footwall ore zone, Sanford Hill | 70.0 | 9.03 | |
| 85 | Rich ore, Sanford Hill | | 10.2 | |
| | Rich ore, lens 4, Sanford Hill* | 60.2 | 12.46 | 0.68 |
| | Medium-rich ore, Sanford Hill* | 42.7 | 9.93 | 0.65 |
| | Medium-rich ore, Sanford Hill* | 49.6 | 12.55 | 0.69 |
| 204 | Lean mineralization in hornblendic gabbroic anorthite gneiss, Sanford Hill | 12.0 | 6.00 | |
| | Lean mineralization in Mafic gabbro, Calamity Mill Pond* | 16.6 | 7.02 | 0.81 |
| | Lean mineralization in gabbro, Iron Mtn. (Mt. Adams) | 13.1 | 9.27 | 0.95 |
| | Percent of $TiO_2$ in Accessory Magnetite in Massive Anorthosite for Comparison | | | |
| 220 | Olivine-pyroxene anorthosite, Lake St. John mass, Quebec. Plagioclase = An 59 $Ab_{41}$ | | 7.2 | |

* Balsley, James R., 1943, p. 115.

TABLE 5

Variation in Percent of $TiO_2$ in Titaniferous Magnetite of New Jersey Igneous Rocks and Gneisses*

| | Field no. | Percent $TiO_2$ in titaniferous magnetite |
|---|---|---|
| PYROXENIC SERIES | | |
| (1) Hedenbergite microantiperthite quartz syenite | 1924 | 7.97 |
| (2) Hedenbergite microantiperthite alaskite | 173 | 3.92 |
| (3) Hedenbergite microantiperthite alaskite | 175 | 3.03 |
| (4) Hedenbergite quartz syenite with microantiperthite partly albitized throughout | 1923 | 1.96 |
| (5) Albite-oligoclase alaskite, Hibernia mine | 169 | 2.76 |
| (6) Albite pegmatite, Hibernia mine | 170 | 1.57 |
| (7) Albite pyroxene quartz syenite pegmatite | Ed-401 | 3.67 |
| (8) Albite pyroxene quartz syenite pegmatite | B-131 | 2.75 |
| (9) Film microantiperthite granite pegmatite, slightly albitized | Ed-949 | 1.97 |
| (10) Pyroxene syenite gneiss reconstituted in amphibolite facies | 147 | 0.98 |
| HORNBLENDIC SERIES | | |
| (11) Hornblende alaskite | 172 | 2.70 |
| (12) Biotite alaskite | 171 | 3.28 |
| (13) Accessory in hornblende allanite albite-microcline granite pegmatite | 174 | 1.74 |
| (14) Microcline (slightly perthitic) granite pegmatite | B-193 | 0.89 |

* Taken from unpublished data of Buddington, A. F., and Baker, D. R., U. S. Geological Survey. Analyses 1, 4, 7, 8, 9, and 14 are by the Rock Analysis Laboratory, University of Minnesota.

TABLE 6

Variations in Percent of $TiO_2$ in Titaniferous Magnetite of Magnetite-Ilmenite-Rich Segregations or Ore Bodies

| Associated rock and locality | Percent $TiO_2$ in magnetite |
|---|---|
| **WITH OLIVINE GABBRO INTRUSIONS** (Titanium compound in magnetite is ferrous-iron-rich mineral) | |
| Magnetite olivinite, Susimäki, Finland[1] | 25.7 |
| Magnetite concentration with olivine and laboradorite, Sodra Ulvön, Sweden[2] | 20.2 |
| Magnetite olivinite, Taberg, Norway[3] | 18.1 |
| Cumberlandite, Rhode Island[4] | 20-25 |
| **WITH LAYERS OF OLIVINE-RICH GABBRO IN STRATIFORM SHEETS** | |
| Duluth gabbro, Minn.[5] | 15-20.8 |
| Skaergaard complex (titanium minerals in magnetite are ulvöspinel and ilmenite)[6] | 19.3-23.8 |
| **IN PYROXENITIC FACIES OF GABBRO** | |
| Pine Lake, Ontario[7] | 18.1 |
| **IN ANORTHOSITE** | |
| Olivine anorthosite, Quebec[8] (titanium mineral in magnetite is ulvöspinel) | 20.2 |
| Rich ore, Sanford Hill, N. Y.[9] | 10-14.5 |
| Iron Spring and Shasta Ranch, Wyoming[10] | 13.2 |
| Mawili, Mozambique[11] | 12-15.4 |
| **IN GABBRO** | |
| Bad Vermillion Lake, Quebec[13] | 23-24.4 |
| Riviere Des Rapides, Quebec[13] | 19.8 |
| St. Charles prospect, Quebec[13] | 13.8 |
| Degrosbois, Quebec[13] | 12.6 |
| **IN GABBRO-DIORITE** | |
| Romsoy, Norway[12] | 8 |
| **IN HORNBLENDITE** | |
| Podesta, Argentina[14] | 6.30 |
| Haines, Alaska[15] | 3.91 |
| Klukwan, Alaska[16] | 3.6 |
| Finland[17] | 4.50 |
| **AS VEINS IN ANORTHOSITE OR GABBRO** | |
| Pyroxene-magnetite-ilmenite vein with crustified structure, in anorthosite, Hayes Prospect, Newfoundland | 3.16 |
| Apatite-magnetite-ilmenite vein in gabbro, Eagle Lake, Quebec[13] | 4.97 |
| **AS VEINS IN GRANITE PEGMATITE AND ALASKITE** | |
| As abundant knots or as segregations, Adirondacks and N. J. | 1.6-3.7 |
| Magnetite lenses with apatite and ilmenite in microperthite alaskite, Adirondacks | 3.9-4.3 |

| IN METAMORPHIC AMPHIBOLITE | |
|---|---|
| Otanmäki, Finland, clinochlorite gangue mineral [18] | 2.5 |

[1] Palmunen, 1925.
[2] Mogensen, 1946.
[3] Hjelmquist, 1950.
[4] McMillan, Heindl, and Conley, 1952.
[5] Grout, 1949-1950.
[6] Vincent and Phillips, 1954.
[7] Pope, 1899.
[8] Girault, 1953.
[9] Balsley, 1943.
[10] Frey, 1946.
[11] Legraye, 1940.
[12] Robinson, 1922.
[13] Foslie, 1913.
[14] Bassi, 1952.
[15] Knopf, 1910.
[16] Wells and Thorne, 1953.
[17] Pehrmann, 1927.
[18] Vaasjoki, 1947.

TABLE 7

Percent of $TiO_2$ in Accessory Magnetite
Gettysburg Sill and Miscellaneous Rocks

| Sample no. | Gettysburg sill, Dillsburg, Pa. | Percent $TiO_2$ |
|---|---|---|
| 217 | Pyroxene diabase | 16.6 |
| 225-a | Pyroxene diabase with interstitial granophyre, slightly coarser than No. 217 | 17.3 |
| 225-c | Pegmatitic facies of diabase with interstitial granophyre | 21.1 |
| 225-b | Red pyroxene granophyre | 7.0 |
| 218 | Red pyroxene granophyre | 11.1 |
| | **Miscellaneous** | |
| 222 | Augite-biotite oligoclase syenite, Larvik, Norway | 17.6* |
| | Giants Range granite, Minnesota (from Bleifuss) | 5.3 |
| 221 | Pink biotite microcline-oligoclase granite, Westerly, R. I. | 0.89 |
| 224 | Biotite-sanidine trachyte porphyry, near Salida, Chaffee County, Colo.** | 6.7 |

New data added while in press; a chemical analysis of a homogeneous one phase magnetite concentrate from a rhyolitic pumice of Valles Grandes, New Mexico submitted by C. S. Ross, has 10 percent $TiO_2$ and can be recomputed to 78.8 percent $Fe_3O_4$, 20.92 percent $FeO.TiO_2$ and 0.28 percent FeO. An X-ray of the analyzed concentrate showed some ilmenite as a contaminant.

* The ilmenomagnetite, in addition to having many coarse parallel lamellae and a grid of coarse and fine ilmenite, also has coarse grains of ilmenite. The interpretation of the latter is uncertain.

** Numerous alteration aggregates with cloud of iron ore particles, pseudomorphous probably after mafic mineral.

### VARIATION OF $TiO_2$ IN MAGNETITE WITH CHEMICAL COMPOSITION OF SYSTEM

Ramdohr (1952) has pointed out the significance of the degree of oxidation of iron in affecting the distribution of titanium between magnetite and a mineral of the ilmenite-hematite solid-solution series. Evrard (1949) has emphasized the importance of oxidation-reduction reactions with magmatic differentiation.

Vincent and Phillips (1954) have interpreted the alternative development of ulvöspinel or of ilmenite as a consequence of oxidation-reduction relationships effected by the respective interstitial magma solutions and have inferred

that this is dependent upon the concentration, or pressure, of water vapor, which controls the state of oxidation of the iron in the iron-titanium oxide minerals even after their initial crystallization. Vincent suggests as one possibility that the amount of interprecipitate liquid in the melanocratic layer was less than that in the average rock and that the amount of iron-titanium oxides in the melanocratic band was so great that the available pressure of oxygen was insufficient to maintain them in a high state of oxidation. This principle may have wide application.

Vincent and Phillips (1954) have presented evidence which they think shows that the percent of $TiO_2$ in magnetite may vary dependent upon the composition of the system in which it forms, and independent of temperature. The data (table 8) taken from their work show that in two facies of the same rock so close together that significant differences of temperature are improbable the percent of $TiO_2$ in magnetite may vary with the composition of the compounds which were dissolved in the magnetite. Where the percent of "ulvöspinel" in the magnetite is large relative to ilmenite—as in the melano-

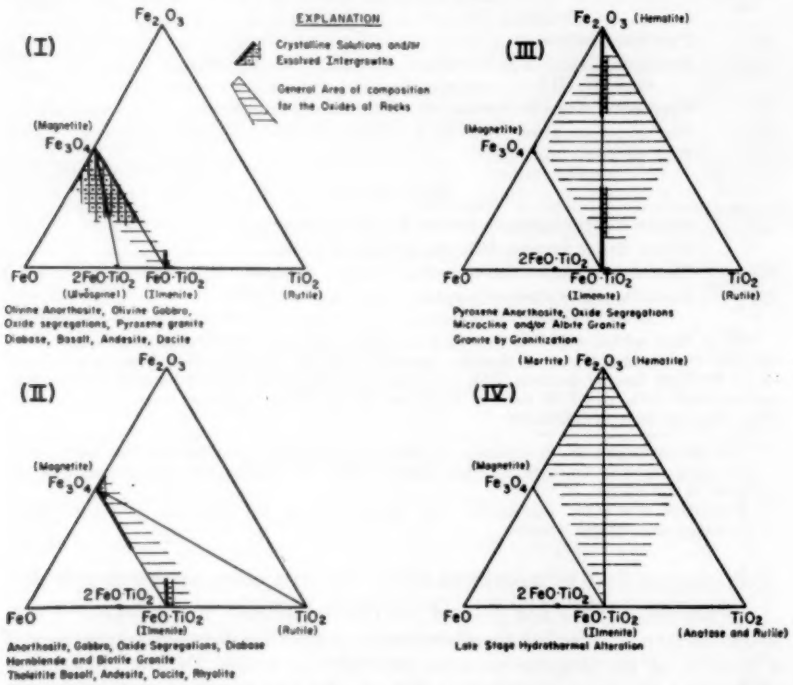


Fig. 1. Diagram, somewhat schematic, to show variation in mineral assemblages with increasing intensity of oxidation. The degree of solid solution indicated is the maximum for the oxides of the specimens upon which the diagrams are based; in II the maximum for ilmenite in magnetite is in the magnetite of diabase whereas the magnetite of granite may have much less $FeO.TiO_2$. Inequilibria or slightly different equilibria are involved in the different possible assemblages of IV.

TABLE 8

Variation of Composition of Magnetite in Skaergaard Complex, Melanocratic vs. Normal Facies*

| | | Volume percent magnetite | Weight percent $TiO_2$ in magnetite | Weight percent $2FeO.TiO_2$ in magnetite | Weight percent $FeO.TiO_2$ in magnetite | Weight percent $Fe_2O_3$ in associated ilmenite | Weight percent $V_2O_3$ in magnetite |
|---|---|---|---|---|---|---|---|
| Hortonolite ferrogabbro | Normal facies | 1.8 | 17.16 | — | 30.80 | — | 0.32 |
| | Melanocratic facies | 21.4 | 23.74 | 24.40 | 28.48 | 4.25 | 0.40 |
| Hypersthene olivine gabbro | Normal facies | 6.6 | 15.40 | 16.32 | 18.13 | — | 1.59 |
| | Melanocratic facies | 36.3 | 19.28 | 43.39 | 7.14 | 2.58 | 1.74 |

* Taken from Vincent and Phillips (1954).

cratic facies—the percent of $TiO_2$ in the magnetite is also larger than where the compound in solution is largely $FeO.TiO_2$. It may be noted, however, that if the concentrations were the product of accumulation of an early oxide segregate, the titaniferous magnetite in the normal layers could have formed at slightly lower temperatures.

## CONSTITUTIONAL DIAGRAMS

Three components: FeO, $Fe_2O_3$, and $TiO_2$ are fundamentally involved in the problem of our titaniferous magnetites.

The kind of minerals constituting an oxide mineral assemblage may vary dependent upon the intensity of oxidation. It may be deduced from the successive diagrams of figure 1 that an oxide assemblage with the same ratio of Fe to Ti may consist (I) of magnetite (with exsolved ulvöspinel) and ilmenite; (II) magnetite (with exsolved ilmenite) and ilmenite with or without rutile; (III) magnetite, ilmenite (with exsolved hematite intergrowths) and titanhematite (with exsolved ilmenite intergrowths); and (IV) magnetite, martite and ilmenite (in part altered to a microaggregate of rutile, anatase and hematite). In part the successive assemblages represent formation at successively lower temperatures but this is not necessarily so.

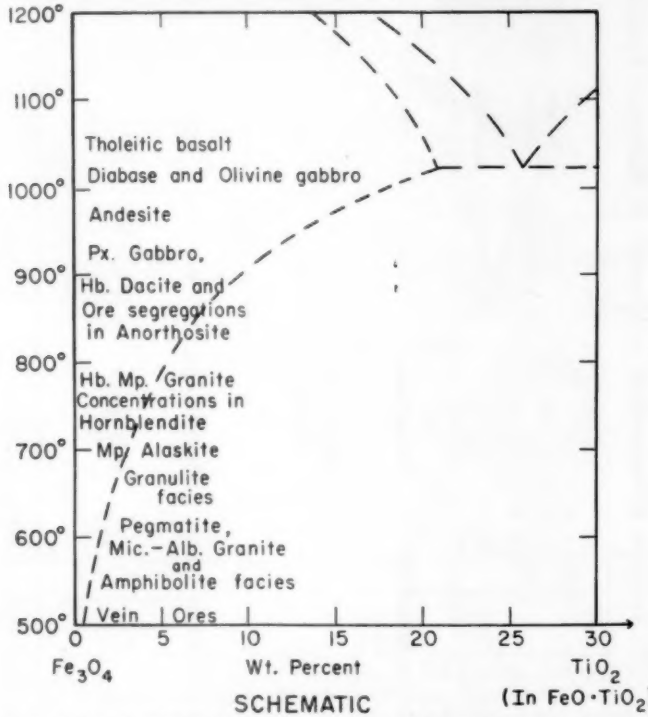


Fig. 2. Inferred relationships for percent of $TiO_2$ in magnetite where $TiO_2$ is in $FeO.TiO_2$ in magnetite and is also present as separate grains.

Ramdohr (1925) has suggested that the temperature-composition diagram for the solidus-liquidus relationships of $Fe_3O_4$—$FeO.TiO_2$ belongs to the type in which there is limited solid solution with a minimum and that the solvus shows limited solid solution with a maximum. A schematic diagram based on this hypothesis is given in figure 2. The solvus of this diagram is based on and adjusted to fit inferred temperatures of formation of the rocks and the known composition of their contained magnetite, where ilmenite is present as distinct separate grains. The inferred temperatures can only be approximate and may not be better than $\pm 100°$ C. The effect of pressure has not been taken into account but is thought to be small.

Data upon which to base a diagram for the relationships of $Fe_3O_4$—$2FeO.TiO_2$ with or without FeO are lacking. Vincent and Phillips (1954, p. 8) state that "The magnetite described by Mogensen (1946) contained 52 percent $Fe_2TiO_4$ (equivalent to 18.4 percent $TiO_2$) and became homogeneous on heating to 600°C." This would necessitate that the solvus curve for the system $Fe_3O_4$—$2FeO.TiO_2$ should lie very much below that of the system $Fe_3O_4$—$FeO.TiO_2$. It further follows that if this is true then for the same temperature, within a broad temperature range, the $TiO_2$ in titanmagnetite crystallizing from a magma where $2FeO.TiO_2$ is available may be much higher than where $FeO.TiO_2$ is entering into the titanmagnetite. It must be emphasized, however, that if the titanmagnetite is to be saturated with $2FeO.TiO_2$ at the given temperature the latter compound would have to be present in adequate amount. The magnetite of most of the Japanese volcanic rocks (table 1) has such a composition that the $TiO_2$ compound can be largely computed as $2FeO.TiO_2$. The magnetite of some of the volcanic rocks is so rich in FeO that there is substantial excess even after recomputation of the $TiO_2$ in terms of $2FeO.TiO_2$. Yet, curiously enough, the amount of $TiO_2$ in the magnetite in general decreases in similar fashion through the series basalt and diabase, andesite, dacite, and rhyolite or granite, no matter what the ratio of FeO is in excess of $FeO.TiO_2$.

In the Adirondacks a varied series of rocks has been reconstituted in the higher temperature portion of the range for metamorphism. The recrystallized titaniferous magnetite varies from a variety with considerable FeO in excess above that necessary to form ilmenite to one with some $Fe_2O_3$ in solid solution. No corresponding systematic variation for the percent of $TiO_2$ in the magnetite, however, could be found.

Ilmenite may occur in large grains coordinate with magnetite that has only $2FeO.TiO_2$ in solid solution as in the anorthosite (no. 220, table 4-A). Furthermore, ilmenite associated with ferrous-iron-rich magnetite may be composed partly of $Fe_2O_3$ (Akimoto, 1954, p. 4).

The whole problem of the system $Fe_3O_4$—$FeO.TiO_2$—FeO with or without $Fe_2O_3$ needs so much additional data that further discussion here is unwarranted.

Two contrasted relationships are inferred from the studies of the natural oxides for the variation of $TiO_2$ in magnetite with temperature. In one case the percent of $TiO_2$ in magnetite *increases* with falling temperature and in

the other case the percent of $TiO_2$ in the magnetite *decreases* with falling temperature.

### DECREASE OF TEMPERATURE WITH INCREASE OF $TiO_2$ IN MAGNETITE

Possible examples of increase of percent of $TiO_2$ in magnetite with decrease of temperature are shown below in table 9. It is inferred that the younger facies of each of the three suites of rocks formed at lower temperatures than the older facies. The younger lower temperature facies would be the fayalite ferrogabbros in the Skaergaard suite, the andesite groundmass of the Japanese rocks, and the pegmatite facies of the diabase. We believe that any interpretation of these data requires a coprecipitation of ilmenite and titaniferous magnetite during a period of crystallization with *falling* temperature and with the titaniferous magnetite phase becoming richer in $TiO_2$. This conceivably could occur in a polycomponent melt of which compounds corresponding to titaniferous magnetite, ilmenite, ferrousorthotitanate, and perhaps oxygen are a part. Ilmenite would bear a reaction relationship toward ferrousorthotitanate until the latter disappeared. At the last stage the relationships for *cotectic* crystallization of titaniferous magnetite and *ilmenite* would hold approximately, and the percent of $TiO_2$ in magnetite would then decrease with a decrease of temperature, in accordance with the solvus curve (fig. 2). Ferrousorthotitanate occurs in the magnetite of the early members of each of the three series given in table 9 but not in the last members.

TABLE 9

General Increase of $TiO_2$ and Decrease of Vanadium in Magnetite with Progressive Crystallization in Mafic Magmas

| | Percent $TiO_2$ in magnetite | Percent $V_2O_5$ |
|---|---|---|
| **Superposed stratiform layers of Skaergaard complex*** | | |
| Fayalite ferrogabbro (2 examples) | 19.68 | nil |
| | 28.09 | nil |
| Ferrohortonolite ferrogabbro | 15.08 | nil |
| Hortonolite ferrogabbro | 17.16 | 0.32 |
| Middle gabbro (olivine free) | 16.28 | 1.61 |
| Hypersthene olivine gabbro | 15.40 | 1.59 |
| **Phenocrysts vs. groundmass, Japanese pigeonitic andesites**** | | |
| Phenocrysts (2 examples) | 13.8 | |
| | 12.3 | |
| Groundmass (3 examples) | 15.8 | |
| | 16.8 | |
| | 20.2 | |
| **Diabase vs. pegmatitic diabase, Gettysburg sill** | | |
| Diabase (2 examples) | 16.6 | |
| | 17.3 | |
| Diabase pegmatite | 21.1 | |

* Vincent and Phillips (1954).

** Iwasaki and Katsura (1950).

The reaction relationship may be the result of oxidation whereby ulvöspinel yields $Fe_3O_4$ and $FeO.TiO_2$. It is also possible that in systems of certain compositions $2(FeO.TiO_2)$ decomposes in the melt to yield $2FeO.TiO_2$ and $TiO_2$; on cooling the reverse reaction may take place. The possibilities are then analogous to those which obtain in the case of magnesian olivine, pyroxene, and silica, where differentiation by fractional crystallization occurs.

If titanmagnetite alone is involved, fractional crystallization could also lead to earlier members being richer in $TiO_2$ (in either $2FeO.TiO_2$ or $FeO.TiO_2$) than later members.

*Skaergaard gabbro complex.*—Vincent and Phillips (1954) have shown that in successively superposed layers of the Skaergaard complex the percent of $TiO_2$ in the magnetite in general increases and the percent of $V_2O_3$ decreases. The lower layers are interpreted (Wager and Deer, 1939) as crystal accumulates formed at higher temperatures than the superposed layers. Vincent and Phillips (1954) have interpreted the variation of $TiO_2$ and $V_2O_3$ in the magnetite to result from magmatic crystallization of mixtures lying on a thermal surface sloping toward a valley in the liquidus surface for the iron-titanium oxides, and proceeding with increasingly titanium-rich magnetite crystallization as consolidation progressed towards lower temperatures. The composition of the magnetite in the ferrohortonolite ferrogabbro is anomalous, and no explanation was advanced. They further suggested, however, that the ilmenite in discrete grains in the lower layers was actually exsolved from the magnetite. *If* this is the case, then a systematic relationship of the type under discussion is not present.

*Japanese pigeonitic andesites.*—In table 9 the data of Iwasaki and Katsura (1950) show that in certain andesites of the pigeonitic rock series as defined by Kuno (personal communication) the titaniferous magnetite phenocrysts have a lower percent of $TiO_2$ than the groundmass magnetite. This would be consistent with crystallization of the phenocrysts at a higher temperature than the groundmass.

*Diabase of Gettysburg sill.*—The pegmatitic facies of the diabase in the Gettysburg sill has a slightly more sodic plagioclase, a slightly more calcium- and iron-rich pyroxene, and more interstitial granophyre than the associated diabase (Hotz, 1953, p. 689). This is in accord with a lower temperature of crystallization for the pegmatite. The percent of $TiO_2$ in the magnetite of the pegmatite is higher than in that of the diabase. The magnetite of the pegmatite carries $Fe_2O_3$ in solid solution whereas the magnetite of the diabase has some ferrousorthotitanate.

### DECREASE OF TEMPERATURE WITH DECREASE OF $TiO_2$ IN MAGNETITE

Although the geologically inferred temperature ranges of formation of the rocks give only crude approximations, nevertheless they do indicate that qualitatively the igneous rocks basalt and diabase; andesite and gabbro; dacite, rhyolite, granophyre and microperthite or microantiperthite granite; and microcline-plagioclase granite and granite pegmatite formed in successively lower ranges of temperature. There is a corresponding decrease in the range of amount of $TiO_2$ in the titaniferous magnetite of these rock groups

(tables 1, 10, and 11). The temperature ranges given in table 10 are for the *rocks* which will include, but not necessarily be the same, as that for the formation of the magnetite.

TABLE 10 VARIATION OF COMPOSITION OF TITANIFEROUS MAGNETITE WITH NATURE OF ROCK AND TEMPERATURE

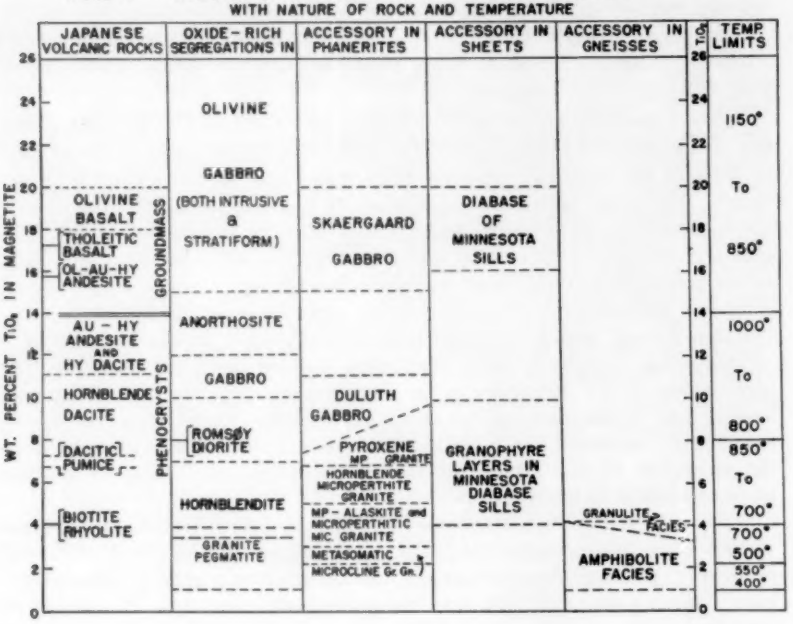


TABLE 11

General Decrease of $TiO_2$ and of $V_2O_3$ in Magnetite with Increase of Silica, Japanese Volcanic Rocks*

| | Percent $TiO_2$ | Percent $V_2O_3$ | Percent MnO |
|---|---|---|---|
| Average 4 magnetite in basalt | 15.70 | 0.96 | 0.79 |
| Average 3 magnetite in andesite | 9.28 | 0.51 | 0.76 |
| Magnetite in hornblende-augite dacite | 11.14 | 0.36 | 0.75 |
| Magnetite in liparite | 4.06 | 0.25 | 1.22 |

* Based on Taneda, S. (1950).

In the metamorphic rocks representing facies reconstituted in different temperature ranges in solid state there is also a diminution in the $TiO_2$ content in magnetite with decrease of temperature. This diminution may be shown by the higher $TiO_2$ content (3.3-4.0 percent) in magnetite of rocks of both the granulite and the higher temperature part of rocks reconstituted in the

amphibolite facies as compared with the $TiO_2$ content in magnetite (3-1 percent) of rocks reconstituted in the lower temperature of the amphibolite facies.

However, certain granitic and rhyolitic rocks crystallized from magma may form in the same temperature range and have a titaniferous magnetite similar to that formed in the solid rock of the granulite facies. Anhydrous granitic rocks may be solid in the same temperature ranges where they are at least partly liquid and magmatic if they contain an appropriate percentage of hyperfusibles.

The accessory titaniferous magnetite of the gabbro in table 3 Minnesota contains very little magnetite with as high a $TiO_2$ content as the magnetite of the diabase (table 2). This could be interpreted as a result of the gabbro retaining the volatiles and consequently crystallizing, at least in part, at lower temperatures than the diabase.

The analyses (tables 3 and 3-A) show that the titaniferous magnetite accessory in the gabbro in general carries 7.5 to 10.5 percent $TiO_2$, whereas the magnetite from melanocratic gabbro layers with magnetite-ilmenite concentrations may have from 15 to 21 percent $TiO_2$. Data are not available to determine the degree to which ulvöspinel and ilmenite are present in the magnetites of the different horizons.

The data given in table 6 show that the percent of $TiO_2$ in the magnetite of *ore concentrations* decreases successively where the magnetite occurs in such rock groups as olivine gabbro, peridotite, and olivinite; pyroxene andesine or labradorite anorthosite; diorite; hornblendite; and granite pegmatites. This also is inferred to represent successive decreasing temperature ranges for the formation of the ores.

### DECREASE OF VANADIUM IN MAGNETITE WITH PROGRESSIVE CRYSTALLIZATION AND DECREASE OF TEMPERATURE

A synthetic compound $FeO.V_2O_3$, an iron-vanadium spinel, has been prepared by Mathewson, Spire, and Samans (1931). It has a melting point probably exceeding that of platinum (1773.5° C.). Dunn and Dey (1937, p. 130-131) have proposed that the vanadium in magnetite occurs in the mineral coulsonite, probably $FeO.(Fe,V)_2O_3$, and isomorphous with magnetite. The melting point of magnetite (1591° C.) is considerably lower than that of $FeO.V_2O_3$, and where progressive crystallization of a magma occurs with differentiation the more vanadium-rich magnetite may be normally expected to form at the earlier stages and higher temperature. This is the relationship found by Vincent and Phillips (1954) in the rocks of the stratiform Skaergaard complex (tables 8 and 9), by Schwellnus and Willemse (1944) in the stratiform Bushveld complex (table 12), by Taneda (1950) in Japanese volcanic rocks (table 11), and by us in Adirondack plutonic igneous rocks (table 13).

TABLE 12

Increase of $TiO_2$ and Decrease of $V_2O_3$ in *Ore* with Progressive Crystallization in Bushveld Complex*

| | Percent $SiO_2$ | Percent $Al_2O_3$ | Percent MgO | Percent $Fe_2O_3$ | Percent FeO | Percent $TiO_2$ | Percent $V_2O_3$ | Percent MnO |
|---|---|---|---|---|---|---|---|---|
| Average of 5, Upper band | 3.59 | 2.84 | 0.70 | 59.86 | 10.09 | 18.19 | 0.2 | 0.37 |
| Average of 3, Middle band | 1.59 | 3.36 | 0.75 | 64.09 | 10.82 | 16.56 | 0.5 | 0.25 |
| Average of 5, Lower band | 1.76 | 3.35 | 1.04 | 69.15 | 8.56 | 12.63 | 1.2 | 0.21 |

* Based on data of Schwellnus, C. M., and Willemse, 1944, table 1.

TABLE 13

Decrease of Percent of $V_2O_3$ in Magnetite of Adirondack Plutonic Rocks with Increase of Felsic Character

| No. Samples | | Percent $V_2O_3$ |
|---|---|---|
| 8 | In segregations in anorthosite and gabbro, Lake Sanford area (Balsley, 1943) | 0.48-0.78 |
| 2 | In stratiform accumulates in pyroxene syenite gneiss | 0.15-0.32 |
| 5 | Accessory in pyroxene syenite to pyroxene quartz syenite gneisses | 0.08-0.17 |
| 3 | Accessory in hornblende granite | 0.03-0.11 |
| 3 | In segregation veins in hornblende granite, (Av. $V_2O_3 = 0.09$) | 0.05-0.17 |
| 3 | Accessory in granite pegmatite | 0.11-0.14 |

### TITANIFEROUS MAGNETITE-ILMENITE-RICH CONCENTRATIONS IN ANORTHOSITE MAY BE LARGELY MAGMATIC

The rich titaniferous magnetite-ilmenite concentrations in the anorthosite of the Adirondack area contain a magnetite (10-14.5 percent $TiO_2$) corresponding in composition to the titaniferous magnetite that occurs as phenocrysts (11-14 percent $TiO_2$) in the Japanese pyroxene andesite and dacite; it is slightly higher in $TiO_2$ than the usual titaniferous magnetite accessory in the gabbro of Minnesota (7.5-11 percent $TiO_2$). A reasonable inference is that the iron-titanium concentrations in the anorthosite of the Adirondack area were formed at temperatures corresponding to that of andesitic and dacitic lavas and of gabbroic *magma* and may have been formed directly from magma.

The data of table 6 show that magnetite-ilmenite deposits with anorthosite in areas other than the Adirondack Mountains may also have a titaniferous magnetite of similar composition. The magnetite with the olivine anorthosite in Quebec is exceptionally high in $TiO_2$. The $TiO_2$ occurs dominantly as ulvöspinel in both the ore and in the accessory magnetite (table 4-A) in the olivine anorthosite. The nature of the magnetite in the Quebec ore and rocks is equally indicative of a magmatic origin.

The ilmenite-magnetite ore shoot at the Hayes prospect near St. George Harbour, Newfoundland, has a pyroxenite border along one wall and at each end and occurs in exceptionally coarse andesine anorthosite. In part the pyroxene thus has a crustified structure relative to the magnetite-ilmenite ore. The general structure of the ore shoot is analogous to a zoned pegmatite. The orthopyroxene intergrown with the oxides is $Mg_{77}Fs_{23}$. Augite is also present. The aggregate is coarse grained (0.5 inch), and the magnetite has only 3.16 percent $TiO_2$. The ilmenite has exsolved intergrowths of hematite and a little rutile. The ore shoot suggests a kind of pegmatitic residuum from an anorthositic magma at lower temperature than normal.

The normal ilmenite-ilmenomagnetite deposits in gabbro and anorthosite of the Adirondacks have been inferred to be of magmatic origin by Osborne (1928), Balsley (1943), and Stephenson (1945) on the one hand and of replacement origin by Gillson (1949, p. 1046-1048) and Haffner (quoted in Gillson) on the other hand. The present data indicate that the deposits formed at magmatic temperatures. This does not preclude their having been emplaced to some degree by replacement.

Ramberg (1948) and DeVore (1953) have each suggested the possibility that the deposits are the result of metamorphic differentiation. The implications of the composition of the titaniferous magnetite in the deposits in anorthosite, however, are that it formed at a higher temperature than is possible for metamorphic differentiation in the Adirondack felsic rocks in the solid state, as suggested by Ramberg. The felsic rocks would have been molten, and all the rocks would necessarily have been at a distinctly higher temperature than the inferred temperature of metamorphism of the Adirondack anorthositic rocks. The accessory magnetite of the metamorphosed anorthositic rocks carries less than 5 percent $TiO_2$, whereas the magnetite of the rich concentrations may have as much as 14.5 percent $TiO_2$. The titaniferous magnetite in some Lake Sanford *concentrate* is reported (Stephenson, 1945, p. 73) to average 10 percent $TiO_2$. The magnetite and ilmenite would have had to move from a regional zone of lower temperature to a locus of concentration of higher temperature. There would also have had to be a differential concentration of vanadium if the ore is assumed to be concentrated from the felsic gneisses and a strong deoxidation to develop the ore concentrations by metamorphic differentiation, for hemoilmenite is still the most common—locally the exclusive—oxide in the anorthositic country rock gneisses. The general geology is also completely in conflict with the idea of development of the deposits by metamorphic differentiation.

### MAGNETITE IN GRANOPHYRE CONSISTENT WITH MAGMATIC ORIGIN

Granophyre, as a part of diabase sills, has been interpreted both as a product of magmatic differentiation of the diabase magma and as the result of replacement and recrystallization of country rock. The composition of the titaniferous magnetite in the granophyre of the Minnesota diabase sills is similar to the titaniferous magnetite of the phenocrysts of Japanese dacite

and rhyolite and is consistent with formation at magmatic temperature. Similarly the magnetite of a diabase from the Gettysburg sill in Pennsylvania has 16-17 percent $TiO_2$ and the magnetite of two specimens of associated granophyre have 7-11 percent $TiO_2$. The granophyre of the Gettysburg sill has been shown by Hotz (1953) to be of magmatic origin. The composition of the magnetite, however, is itself not proof of magmatic origin, for Broderick (1917), Schwartz (1943), and Grout (1949-1950, p. 35) have shown that titaniferous magnetite may be formed in included layers of country rock enclosed in gabbro. The titaniferous magnetite (4-10.4 percent $TiO_2$) of the diabase sills in Minnesota may be more directly related to recrystallization in the presence of interstitial granophyre magma than to the true diabase minerals of earlier crystallization. A detailed study is needed to check this interpretation.

### TITANIFEROUS MAGNETITE OF MICROPERTHITE GRANITE AND ALASKITE CONSISTENT WITH MAGMATIC ORIGIN

The percent of $TiO_2$ in the magnetite of the pyroxene microperthite granite and pyroxene microantiperthite quartz syenite is similar to that in the phenocrysts of the Japanese hornblende dacite lavas. Though some degree of undercooling may have been involved in the crystallization of magnetite from the magma, the Odawara dacitic pumice with magnetite phenocrysts is proof that the magnetite was in existence as crystals in a lava sufficiently fluid and hydrous (a magma) to be capable of inflation to a pumice.

The composition of ilmenomagnetite from the hornblende microperthite granite is also consistent with a magmatic origin, because it has but very slightly less $TiO_2$ than the magnetite phenocrysts of the Odawara pumice and more $TiO_2$ than the titanomagnetite phenocrysts of the biotite rhyolite from Niizima, Japan. The microperthite alaskites have a magnetite with slightly less $TiO_2$ than the phenocrysts of the rhyolite from Japan. The alaskites crystallized under plutonic conditions where they might be expected to be bathed in residual magmatic fluids for a long time at lower temperatures than rhyolite phenocrysts.

The magnetite of the unmetamorphosed green pyroxene microperthite granite of the Adirondacks carries 8.2 and 9.6 percent $TiO_2$ and that of unmodified pyroxene microantiperthite quartz syenite of New Jersey has 7.97 percent $TiO_2$. These percentages are higher than for any magnetite found in the red hornblende microperthite granites (5.3-6.7 percent $TiO_2$). The green pyroxene granites and quartz syenite are thought to have been formed from magmas with less hyperfusibles (especially $H_2O$) than the red hornblende granites. The magnetite of the hornblende granites has $Fe_2O_3$ in solid solution, whereas the magnetite of the pyroxene granites has no excess $Fe_2O_3$ but on the contrary has in part excess FeO, and the $TiO_2$ mineral in the magnetite is in part ulvöspinel instead of ilmenite. The relatively anhydrous pyroxene granite magma would necessarily have crystallized at somewhat higher tem-

peratures than the hornblende granite magma. The magnetite of the pyroxene granites therefore contains more $TiO_2$, at least partly because of formation at higher temperature.

The mineralogy and geology of the microperthite granites and alaskites are also consistent with a hypothesis of formation from magma.

The potash and soda feldspar in the Adirondack microperthite granites occurs almost exclusively as an intergrowth of the type attributed to exsolution; this proves, in so far as we now know, that these granites must have formed considerably above 600° C. since the plagioclase is an oligoclase. The microperthite granites also formed at temperatures higher than those for rocks of the metamorphic granulite facies, which show the development of coarse-grained pegmatite seams formed by metamorphic differentiation in the solid state (Buddington, 1952). The microperthite granites must, therefore, have formed either in the solid state at temperatures above that of the granulite facies or by crystallization from magma. The texture of the granite is not the polyhedral mosaic type characteristic of metamorphic reconstitution but that of interlocking grains consistent with crystallization from a magma. The hornblende microperthite granite also contains *rotated* angular inclusions of country rock or *far-traveled* inclusions and xenocrysts.

There is a substantial volume of an alaskite in the Adirondacks in which the feldspar is a potash-rich microperthitic microcline. The field relationships led to an interpretation that it formed from magma. The composition of the magnetite is similar to that of the microperthite alaskites. A sodic oligoclase alaskite at the Hibernia mine in New Jersey has been shown by data from a series of drill holes to have a wedge shape and to displace the wall rocks to the extent of its own width. This is consistent with a magmatic emplacement. The magnetite has a percent of $TiO_2$ (2.76) intermediate between that of a microperthite alaskite and that of granite pegmatite.

The systematic variation in the decrease of $TiO_2$ in magnetite (table 14) in rocks such as pyroxene granite and quartz syenite, hornblende microperthite granite, biotite microperthite alaskite, and granite pegmatite indicates that the magnetite is a mineral of contemporaneous crystallization with the silicates rather than one of later stage development alone as advocated by many geologists (Moorhouse, 1953).

If granite forms from magma at temperatures where microcline and albite form independently or if primary magmatic anorthoclase granite is recrystallized at lower temperatures to an aggregate of separate microcline and albite grains, then the associated magnetite may be expected to have a low content of $TiO_2$. This is borne out by the composition of the magnetite of the biotite oligoclase-microcline granite of Westerly, Rhode Island (table 7, no. 221) which has but 0.89 percent $TiO_2$. This is equivalent to the lowest range of microcline granite pegmatite.

TABLE 14

Range of Percent $TiO_2$ in Magnetite of Granitic Rocks

| Samples | Rock | Percent $TiO_2$ in magnetite |
|---|---|---|
| Table 4; nos. 192, 216<br>Table 5; no. 1 | Hedenbergite microantiperthite quartz syenite and ferroaugite microperthite granite | 7.97-9.6 |
| Table 4; nos. 36, 38, 51-S, 79, 100-S, 110-b | Hornblende microperthite granite | 5.3-6.7 |
| Table 5; nos. 2, 3 | Hedenbergite microantiperthite alaskite | 3.0-3.9 |
| Table 4; nos. 37, 39, 64, 142-S, 179, 191 | Microperthite alaskite | 3.1-4.3 |
| Table 5; no. 5 | Biotite fluorite microperthite alaskite | 2.76 |
| Table 4; nos. 176, 180 | Vein deposits of magnetite, ilmenite, pyrite, and apatite in biotite fluorite microperthite alaskite | 3.9-4.3 |
| Table 5; nos. 7, 8 | Segregations or abundant knots of magnetite in pyroxene quartz syenite pegmatite | 2.75-3.67 |
| Table 4; nos. 165, L-2061<br>Table 5; no. 6 | Segregations or abundant knots of magnetite in albite and/or microcline granite pegmatite associated with hornblende or biotite alaskite | 1.57-2.62 |
| Table 4; no. 111<br>Table 5; nos. 9, 13, 14 | Accessory disseminated grains or meager knots in albite and/or microcline granite pegmatite | 0.9-2.3 |
| Table 7; no. 221 | Microcline-oligoclase alaskite | 0.9 |

MAGNETITE OF GRANITE GNEISS FORMED BY GRANITIZATION

Large volumes of microcline-rich granite gneisses in the Adirondacks have been interpreted (Buddington, 1948, p. 36-39) as the product of granitization of a wide variety of country rocks. The composition of the magnetite in such rocks (generally 2.2-3.2 percent $TiO_2$ but may be lower locally) is consistent with this interpretation. The composition of the magnetite is similar to that in gneisses metamorphosed in the temperature range for the intermediate to upper range of the amphibolite facies and to that of granite pegmatite. The magnetite is similar in granitized facies of rocks as dissimilar as biotite quartz plagioclase gneiss, amphibolite, pyroxene skarn, and garnet skarn. The associated ilmenite in the granitized gneisses has exsolved hematite intergrowths.

### TITANIFEROUS MAGNETITE IN GRANITE PEGMATITE

The granite pegmatites have a wide variation in the mode of occurrence and development with a correlated variation in the composition of the magnetite. Two contrasted examples may be cited. The first is a pegmatitic seam of magmatic origin, 2 inches wide, representing merely a coarser, more felsic facies of the microperthite granite in which it occurs. The percent of $TiO_2$ in the accessory magnetite is 5.7, and the feldspar is microperthite. The second is a microcline pegmatite developed as a metamorphic segregation veinlet in solid rock, which itself is a product of granitization of andraditic skarn. The magnetite of the andradite granite gneiss carries 0.86 percent $TiO_2$ and that in the pegmatite only 0.51 percent $TiO_2$. The feldspar is microcline in the granite gneiss as well as in the pegmatite.

The titaniferous magnetite in granite pegmatite in general may vary from a very minor accessory mineral through knots with tentacle-like protrusions to local ore shoots as much as a few score of feet in length. The rock with accessory magnetite is by far the most common. The feldspar of the pegmatite may be almost wholly albite or wholly microcline or a mixture of the two. The potash feldspar may be slightly perthitic. The magnetite of the pegmatites associated with the pink alaskite and granite carries less $TiO_2$ than the magnetite of the alaskite itself or of the transitional alaskites. The pegmatite vein from which the magnetite knots (table 5, no. 14) were taken is well exposed, is 13 feet wide, and transects with sharp borders isoclinally plicated migmatitic amphibolite. It appears to be a *dike* formed by intrusion and consolidation of a magma. The $TiO_2$ in the magnetite is relatively low (0.9 percent) and may have been recrystallized at the last stage of consolidation of the pegmatitic magma.

The magnetite of the green pyroxene quartz syenite pegmatites may carry a higher percent of $TiO_2$ than the magnetite of the pink pegmatite associated with pink hornblende granite or biotite alaskite. This is analogous to a similar relationship between the magnetite of the green pyroxene granite and red hornblende granite.

The percent of $TiO_2$ in the magnetite of the pink granite pegmatites is similar to that in the granite gneisses recrystallized in the temperature range of the amphibolite facies. This would necessitate that the last stages of crystallization of the pegmatitic magma should be in a similar range of temperature. Such low magmatic temperatures are here as usual inferred to be due to a high content of hyperfusibles.

### TITANIFEROUS MAGNETITE OF VEINS AND REPLACEMENTS

There are several small vein-type ore shoots (table 4, nos. 176, 177, 180) in alaskite in the Adirondacks consisting of magnetite, ilmenite, and apatite with some pyrite and a little chalcopyrite. The ore shoots are less than a hundred feet in length, and may locally have selvages of granite pegmatite. Gradations into the normal granite pegmatite were not seen, and there appears to be an effective discontinuity between the nature of the solutions which formed each. They could have formed, perhaps, as an immiscible segregation

from pegmatitic magma (cf. Fischer, 1950). The composition of the magnetite is such as could have been in equilibrium with that in an alaskitic or pegmatitic magma. However, in one such vein the magnetite carries only 1.2 percent $TiO_2$. In this ore the ilmenite grains carry exsolved hematite at the core and are clean on the borders. There is also some late hematite. This ore must have been formed at lower temperatures than the others. The magnetite associated with pyrite either has slight excess FeO over that necessary to form ilmenite or a very low excess $Fe_2O_3$.

Titaniferous magnetite in association with independent ilmenite grains may occur in the form of a replacement as accessory disseminations in gneiss to the extent of several percent (table 4, nos. 74, 166, NP-SA). The percent of $TiO_2$ in the magnetite of the replacement is generally less (1-2 percent $TiO_2$) than is common in the magnetite-rich facies of the pegmatite (1.5-3 percent).

Where the magnetite occurs in greater concentrations and on a larger scale as replacement of gneisses or skarn it is a slightly titaniferous variety (less than 1 percent $TiO_2$). The magnetite of the ore in gneiss at the Benson mines in the Adirondacks usually carries less than 0.5 percent $TiO_2$ and rarely has independent grains of ilmenite. The large-scale development of the slightly titaniferous magnetite replacement veins, however, as contrasted with the small-scale development of the vein deposits with ilmenite is not consistent with a hypothesis that the slightly titaniferous deposits are directly related to the pegmatites. The veins are more probably directly related to the major granite masses.

Kullerud (1953, p. 138) has determined the temperature of formation of the marmatite at Balmat and Edwards in the Adirondacks to be 375° C. and 385° C. respectively for a depth equivalent to 2000 atmospheres. The geologic relationships are consistent with the theory that the magnetite deposits in gneiss formed at higher temperatures, perhaps around 500° C. The vein deposits with ilmenite may have been somewhat higher, and the accessory and segregated magnetite in the simple pegmatite veins still higher, perhaps around 550°-700° C.

### EFFECTS OF LATE MAGMATIC, DEUTERIC, AND HYDROTHERMAL MODIFICATIONS

In a great variety of rocks, the magnetite of concentrations often has a higher percent of $TiO_2$ than the accessory or disseminated magnetite of the associated igneous rock. This is true for segregations in gabbroic stratiform sheets, ore bodies in anorthosite, segregations in hornblendite, and concentrations in granite pegmatite. A possible explanation is that both the magnetite of the concentrations and the disseminated magnetite were initially formed under similar conditions but the disseminated oxides were later modified by late stage residual solutions at lower temperatures, whereas these solutions were inadequate to effect such recrystallization of the concentrations.

The percent of $TiO_2$ in the magnetite of the Minnesota basalts (table 2) ranges in general from 2.5 to 10.2 including 4 samples that range from 2.5 to 3.5. This is in contrast to the higher content (15-20 percent) of $TiO_2$ found

in the magnetite of the groundmass of the Japanese volcanic rocks and in many other basalts and diabase. The difference may lie in a late stage, partial or complete hydrothermal alteration, or pneumatolytic alteration of the magnetite in the Minnesota rocks at temperatures lower than those normal for the magmatic crystallization of the lava.

Bleifuss' data on the magnetite of the Minnesota diabase show that there are two groups of analyses, 7 with 16-20 percent $TiO_2$ and 8 with 4.0 to 10.4 percent $TiO_2$. The first is certainly related to the main period of diabase crystallization; the latter, perhaps, is due to recrystallization by and precipitation in late-stage interstitial granophyric magma.

At Klukwan, Alaska (Wells and Thorne, 1953) the magnetite of rich ore lenses and of lean disseminations in a mass of hornblendite has different percentages of $TiO_2$ respectively as indicated below.

Composition of Magnetite in Hornblendite, Klukwan, Alaska

| Weight percent magnetic concentrate from rock, 200 mesh | Percent $TiO_2$ in magnetic concentrate |
|---|---|
| Disseminations, 9.7 to 17.74 | 1.40-1.65 |
| Rich ore, 76.6 to 81.68 | 3.5-3.6 |

A possible explanation is that though the rich ore concentrations and the disseminations are both of late magmatic origin, late-stage solutions of deuteric character have been present in adequate amount to rework the disseminated magnetite type but not the ore lenses. Part of the titanium of the rock with disseminations is in late-stage sphene that is associated with albite, epidote, and zoisite. The magnetite of both types carries about 0.3 percent vanadium (0.44 percent $V_2O_3$) which is unusually high for a normal hydrothermal vein type of deposit but not unusual if the hornblendite is considered a facies of gabbroic composition crystallized from a magma so exceptionally rich in volatiles that it yields hornblende instead of pyroxene and plagioclase as in normal gabbro.

The magnetite of the partly albitized hedenbergite microantiperthite quartz syenite (table 5, no. 4) has but 1.96 percent $TiO_2$ in contrast to the magnetite of the unmodified primary rock (table 5, no. 1) with 7.97 percent $TiO_2$. The solutions effecting the albitization were either deuteric or hydrothermal, and the primary magnetite was recrystallized by them. The magnetite of the albitized rock is similar to that of the film microantiperthite pegmatite (table 5, no. 9), and the albite-oligoclase alaskite (table 6, no. 169).

The magnetite of two microperthite alaskites (table 4, nos. 178, 187) contaminated with pyroxene has sphene coronas indicative of late-stage relatively low temperature reactions and carries less $TiO_2$ than the normal alaskite.

## ARE ILMENOMAGNETITE-ILMENITE CONCENTRATIONS IMMISCIBLE SEGREGATIONS?

Ilmenomagnetite-ilmenite concentrations occur on the one hand with gabbroic rocks (including anorthosite and hornblendite) both as concordant segregation facies and as discordant bodies, and on the other hand with gran-

itic rocks as segregation facies in granite pegmatite or as small veinlike lenses in alaskite. Many geologists have interpreted certain geologic relationships of the concentrations to indicate that they formed from a mobile fluid. Bateman (1951) has suggested a *residual liquid* for the deposits associated with gabbroic rocks. There is a problem to reconcile this with the hypothesis that a syenitic or granophyric liquid is the residual liquid, as in the Skaergaard and Duluth masses. The possibility that the deposits formed from mobile immiscible segregations, however, has to be considered. The data presented here are taken to imply that the ilmenomagnetite of the concentrations with gabbroic and anorthositic rocks formed at similar temperatures to the accessory ilmenomagnetite of the related silicate-rich host rock. This is consistent with and a necessity for a hypothesis of origin through immiscibility. If the immiscible relationship held only for a severely limited range of chemical composition of the system and a limited temperature interval, analogous to the elliptical type of relationship for immiscibility in a two-component system, it would permit silicate-rich liquids to constitute the sole magma for most of the time in both the early and the later periods of consolidation and differentiation. In the Lake Sanford area, conformable layers of gabbro and pyroxenite in anorthosite may contain facies, again as conformable layers, so enriched in ilmenomagnetite and ilmenite that they constitute ore. The pyroxenitic layers have a stratiform character resembling that of mafic concentrations in the great stratiform sheets. There are many phenomena related to the anorthositic series of rocks which would be consistent with origin from a water-rich magma. An immiscible segregate could similarly be water-rich.

The composition of the ilmenomagnetite of concentrated knots and segregations in granite pegmatite and in certain lenses in alaskite is similar to the accessory ilmenomagnetite in the host rock. This again would be compatible with an immiscible relationship.

Asklund (1949) has advocated the hypothesis that apatite-bearing iron ores such as those of Kiruna are the product of liquid immiscibility with silicate magma. The occurrence of apatite-rich ilmenomagnetite-ilmenite-pyrite veins in the Adirondacks of possible immiscible origin with alaskite magma has already been referred to. Most ilmenite-ilmenomagnetite concentrations in gabbro and anorthosite in general carry only a little apatite, but there are some in which apatite is present in substantial amounts. Jooste (1949) cites one of the St. Charles deposits in anorthosite in Quebec as consisting of 22.2 percent apatite. The associated magnetite carries 12.76 percent $TiO_2$. There are all gradations between the apatite-rich and apatite-poor facies, as though both had a common origin.

There are thus a number of natural phenomena which would be consistent with a hypothesis of immiscible segregation of ilmenite-ilmenomagnetite concentrations from anorthositic, mafic, or felsic magmas, but as there is no adequate experimental supporting evidence, the problem awaits further elucidation.

## MAGNETITE OF METAMORPHIC ROCKS

The development of sphene at the expense of all the ilmenite in some granite gneisses reconstituted in the lower range of the amphibolite facies leaves a magnetite unusually low in titanium. At the other extreme the reconstitution of some metagabbros in the amphibolite facies may leave only ilmenite, whereas the magnetite is wholly taken up by the newly developed hornblende of the resulting amphibolite.

The data given in table 4 for the metamorphic rocks show that the magnetite for a series of gneisses as widely variable as pyroxene granite, pyroxene syenite, hornblende granite, gabbro, and anorthosite has a similar composition (commonly 3-4 percent $TiO_2$) where they have been reconstituted in the garnetiferous granulite facies or in the higher temperature range of the amphibolite facies. Rocks metamorphosed in the lower part of the temperature range for the amphibolite facies have magnetite with 1-3 percent $TiO_2$.

The Adirondack granitic and syenitic rocks of the amphibolite facies vary from those in which the primary microperthite feldspars are recrystallized to microcline and plagioclase to those in which a microperthitic potash feldspar (which may or may not show microcline twinning) is present. There is no garnet but sphene has developed, especially in the microcline gneisses, in consequence of reaction with the silicates of titanium exsolved from the ilmenomagnetite. The percent of $TiO_2$ in the ilmenomagnetite may be the same for part of the rocks developed in the amphibolite facies *and* for those formed in the granulite facies. This may, nevertheless, have occurred at the same temperature, but at different pressures, the granulite facies having formed at the same temperature but at greater depth than the amphibolite facies with ilmenomagnetite of the same composition. This is consistent with a reasonable interpretation of Adirondack geology based on independent data (Buddington, 1952).

## CONCLUSION

In conclusion, it is recognized that until we have very much more data on the composition of all kinds of titaniferous magnetites in all kinds of rocks, until we have systematic experimental data on pertinent solubility and polymorphic phenomena, and until we have a better understanding of the effect of the physicochemical history of the system in controlling the composition of the magnetite, any interpretations we may make can be but a first approximation to the real story. Nevertheless, we believe that it is demonstrated that variations in the composition of titaniferous magnetite have potentialities of becoming an important element in geologic thermometry for temperature ranges between 550° C. and 1000° C. and in the interpretation of the physicochemical history of many rocks.

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# RATE OF WATER REPLACEMENT IN A BAY OF LAKE MENDOTA, WISCONSIN

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ABSTRACT. Measurements of rates of wind-driven water replacement for a bay are reported. Replacement by both vertical motion and horizontal eddying is present. Since the replacement by vertical motion is proportional to the wind, it varies from a few hours to several hundred hours for the surface meter. The horizontal circulation seems to be by eddies of the dimension (and circulation rate) of inertia circles. Associated with the circulation of the bay is a relatively narrow "jet stream" along one side of the bay, the velocity of which is proportional to the cross-bay component of the wind.

## THE EXPERIMENT

During the spring of 1952, the fall of 1953, and the summer of 1954, a line of eight stations was established across the mouth of University Bay, Lake Mendota, Wisconsin. The currents at various depths were measured by the drag method (Putnam, Munk, and Taylor, 1949), using either a taffrail log or a rangefinder for distance measured. The velocity components normal to the line of stations, i.e. into or out of the bay, were computed and processed to yield horizontal divergence rates for the entire bay at each level.

The divergence of a layer is measured by the export or import across the mouth of the bay. If there is net outflow across the mouth of the bay, this must be compensated by vertical motion or replacement within the bay to maintain a constant water level in the bay. For ease of interpretation, the time required for complete replacement of a layer will be used rather than the rate.

## REPLACEMENT TIMES FOR VERTICAL MOTIONS

Replacement times varied from about 3 hours to more than 600 hours (table 1). It must be borne in mind, however, that the replacement times are computed from a series of current measurements made over an hour or so. A replacement time of 6 hours does not mean necessarily four complete renewals of the water in one day, for the *rate* can and does change rather rapidly with the wind. For example, on 8 July, 1954, the computed replacement time for the upper 5 meters of water was 214 hours, but 24 hours later the replacement time had changed to 20 hours.

The rate of replacement of the upper layers is a function of the down-bay component of the wind, for the replacement time is proportional to the mean velocity of the water across the bay mouth, and this in turn is related linearly to the down-bay component of the wind (fig. 1). At greater depths, wind effects are reduced and pressure gradients play a greater role (Bryson and Suomi, 1952) as indicated by the smaller variability of replacement times at 10 meters (table 2).

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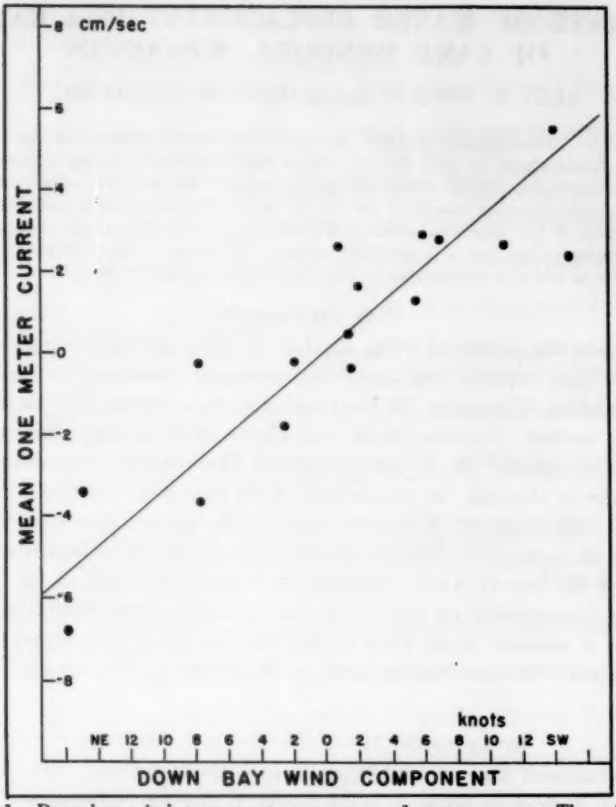


Fig. 1. Down-bay wind component versus mean 1 meter current. The winds were measured at Truax Field near Lake Mendota, but are probably representative for the lake.

TABLE 1
Summary of Replacement Times and Mean Outward Velocity Components for University Bay

| Date | Mean velocity divergence x $10^{-5}$ x $sec^{-1}$ | Thickness of surface layer used (meters) | Replacement time (hours) | Mean outward velocity cm/sec 1 m | Wind velocity mph | Direction |
|---|---|---|---|---|---|---|
| 1 July, 1954 | +1.67 | 1 | 17.0 | +1.30 | 6-8 | W |
| 30 June, 1954 | -0.44 | 1 | 77.0 | - .34 | 13 | NW |
| 29 June, 1954 | +3.34 | 1 | 9.7 | +2.60 | 14 | W |
| 28 June, 1954 | +3.83 | 1 | 7.2 | +2.98 | 8 | S |
| 26 June, 1954 | -0.23 | 1 | 120.0 | - .189 | 13 | NW-NE |
| 25 June, 1954 | +7.00 | 1 | 4.0 | +5.45 | 15 | SSW |
| 24 Nov., 1953 | +3.30 | 1 | 8.4 | +2.57 | 15 | NW |
| 24 Apr., 1952 | -4.34 | 1 | 6.5 | -3.38 | 15 | NE |
| 23 Apr., 1952 | -8.70 | 1 | 3.2 | -6.78 | 15-20 | ENE |
| 22 Apr., 1952 | -2.26 | 1 | 12.0 | -1.76 | 3-5 | N |
| 19 Nov., 1953 | +3.64 | 1 | 7.6 | +2.84 | 10-12 | S |
| 30 Oct., 1953 | +2.64 | 2 | 10.0 | +2.22 | 15 | SW |
| 7 July, 1954 | -5.49 | 5 | 5.1 | -3.56 | 12 | N |
| 8 July, 1954 | -0.04 | 5 | 690.0 | + .23 | 3 | WNW |
| 9 July, 1954 | +1.39 | 5 | 20.0 | +1.75 | 3 | S |
| 16 July, 1954 | -0.78 | 5 | 36.0 | - .20 | 1-5 | N |

TABLE 2
Replacement Times in Hours at Various Depths

| Date | 1 m | 2 m | 5 m | 10 m |
|---|---|---|---|---|
| 7 July, 1954 | 5.5 | 3.5 | 8.3 | 10.1 |
| 8 July, 1954 | 82.0 | 252.0 | 57.0 | 7.9 |
| 9 July, 1954 | 10.0 | 32.0 | 46.0 | 20.0 |
| 14 July, 1954 | — | — | 25.0 | 17.0 |
| 16 July, 1954 | 90.0 | 14.0 | 695.0 | 17.0 |

## THE PICNIC POINT JET

The authors had observed on many occasions prior to this study that there existed a narrow strip of rapidly moving water leaving University Bay along the south side of Picnic Point, the peninsula bounding the bay on the north. This phenomenon is clearly shown on the profiles of water velocity components normal to the bay mouth (fig. 3). That this is not an isolated occurrence is indicated by the fact that it is present on the mean velocity profile as well (fig. 2). It has been identifiable on every profile of velocity which has been made.

Unlike the mean velocity normal to the bay mouth, the velocity of the jet is found to be proportional to the cross-bay wind component, but the factor of proportionality seems to be different with a north-west component than with a southeast component (fig. 4). Furthermore, the core of the jet is closer to Picnic Point with a southeast component and more distant with a northwest component. In the latter case there is often a narrow countercurrent between the jet and the shore of Picnic Point. These facts suggest that different processes are operative in the two cases.

As may be seen from the mean chart (fig. 2), there is normally an anticyclonic eddy in University Bay. The evidence presented in this paper and others (Bryson and Suomi, 1952; Ragotzkie and Bryson, 1953) shows that this eddy is wind-driven, and thus the outward flow on the north side of the bay would be proportional to the wind.

In the case of a northwest wind, the main portion of the lake and University Bay behave as two separate basins from the point of view of stratification. The isotherms are depressed and the thermocline sharpened downwind, while rising toward the surface upwind. Therefore, off the tip of Picnic Point a discontinuity is observed, for it is upwind for University Bay and downwind for the main portion of the lake (Bryson and Suomi, 1952, fig. 2). The tilt of the surface across the discontinuity would produce a slope current into the bay and the relative current due to the slope of the isotherms would be similarly directed. This effect would run counter to the normal outflow and is the probable cause of the countercurrent and reduced jet velocity near Picnic Point. With a southeast wind the slope and relative currents at the discontinuity would add to the normal wind-driven outflow in the neighborhood of the Point, thus giving higher velocities in that region (fig. 4).

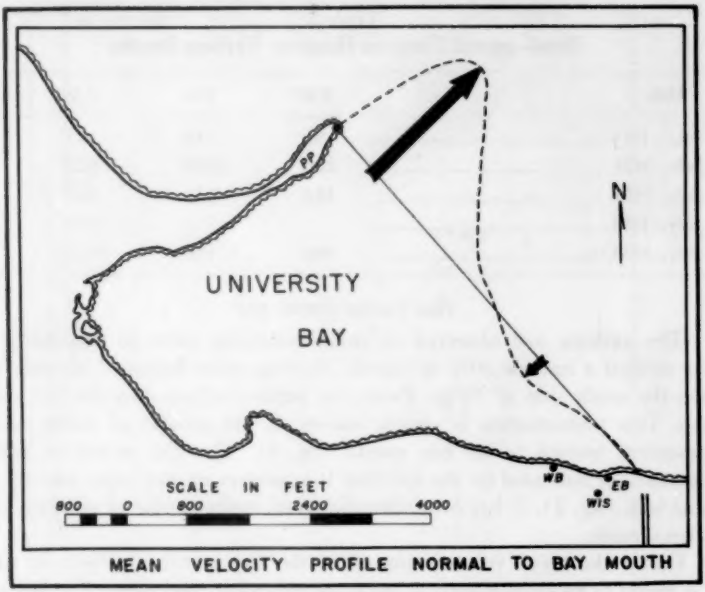


Fig. 2. Mean current profile normal to bay mouth at 1 meter depth. Transport per 10,000 seconds is shown. PP indicates Picnic Point.

## HORIZONTAL EDDIES

Referring back to figure 2, it may be seen that there is another mode of water replacement, i.e. by purely horizontal exchange—export on one side of the bay and replacement by import on the other side. This effect is superimposed on the divergence discussed in previous sections of this paper.

In University Bay, replacement of this type usually is accomplished by maximum outflow along Picnic Point, in and along the jet which has been described, and secondarily in a narrow region along the south shore of the bay. In the surface layer the location of the region of maximum inflow varies with the maximum outflow velocity along Picnic Point. Such a pattern suggests an eddy whose size varies with the velocity around the eddy, a characteristic of inertia circles. To examine the possibility of inertial flow the following procedure was adopted: From the arithmetic average of the velocity maxima into and out of the bay the radius of the appropriate inertia circle was calculated. Half the distance between the two velocity maxima was taken as the observed radius.

The correspondence between the calculated and observed radii is an indication, at least, of whether inertial flow actually occurs (fig. 5). The good agreement found between the two radii indicates that high inflow and outflow velocities are associated with large eddies (or gyres if the word may be used in a limnological sense) which are largely inertial in character in the surface layers. This affords us an estimate of the rate of replacement by strictly horizontal exchange. For the two halves of an inertia circle or gyre to exchange

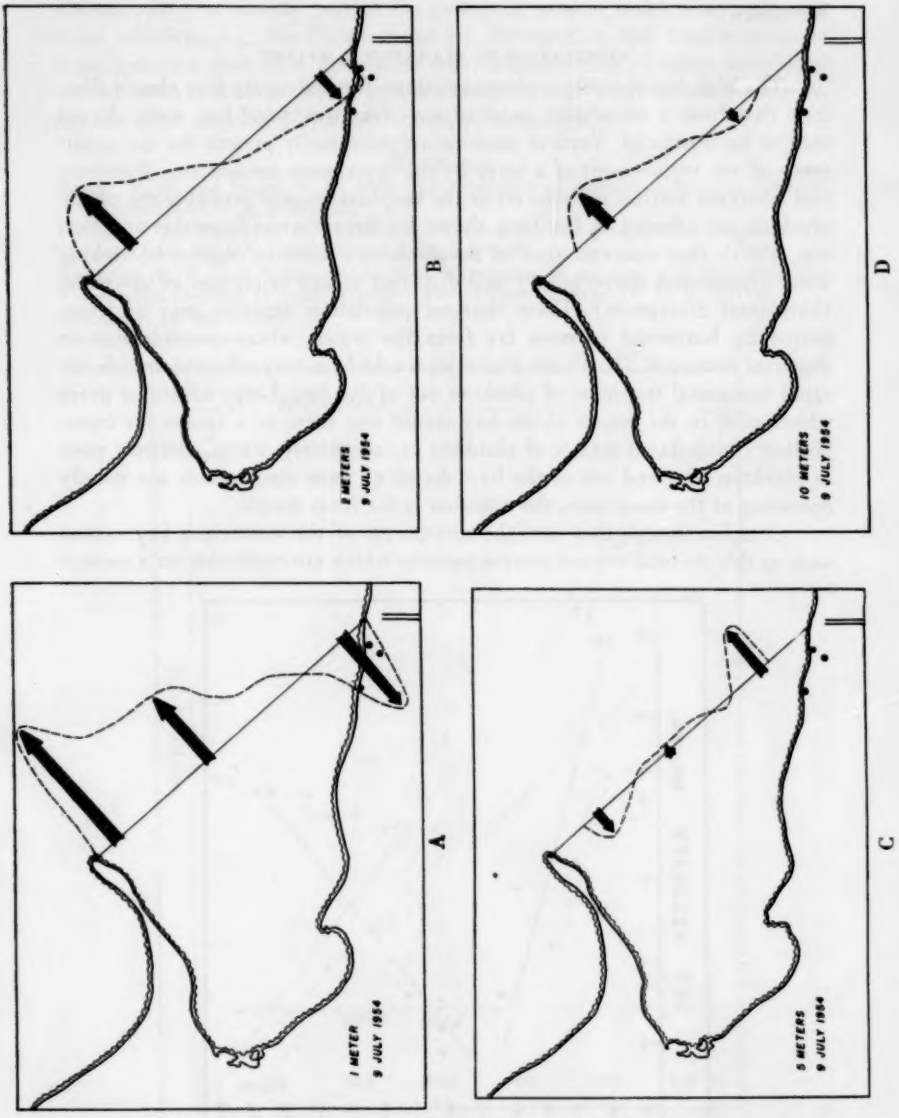


Fig. 3. Current profiles normal to bay mouth, July 9, 1954. Transport per 10,000 seconds is shown. Scale, etc., as in figure 2.

A. At 1 meter depth.
B. At 2 meter depth.
C. At 5 meter depth.
D. At 10 meter depth.

requires one-quarter pendulum day or 8½ hours at the latitude of Madison, Wisconsin.

### APPLICATION TO PLANKTON SAMPLING

The high but variable replacement times for University Bay clearly illustrate that from a circulation point of view lake water and bay water do not tend to be separated. Vertical motions are necessarily present for the occurrence of net replacement of a layer by the divergence mechanism. Whenever and wherever vertical motions occur the zooplankton and probably the phytoplankton are affected. It has been shown by the authors (Ragotzkie and Bryson, 1953) that concentration of zooplankton occurs in regions of sinking water (horizontal convergence) and dispersal occurs in regions of upwelling (horizontal divergence). These changed population densities may be transported by horizontal currents far from the region where concentration or dispersal occurred. The Picnic Point jet would be a very effective vehicle for rapid horizontal transport of plankton out of the bay. Large eddies or gyres which exist in the mouth of the bay would also serve as a means for transporting concentrated masses of plankton or, alternately, water relatively poor in plankton into and out of the bay. As all of these mechanisms are usually operating at the same time, the situation is far from simple.

Complex though they are, the movements of the water in a bay system such as this do tend toward certain patterns which are explicable on a reason-

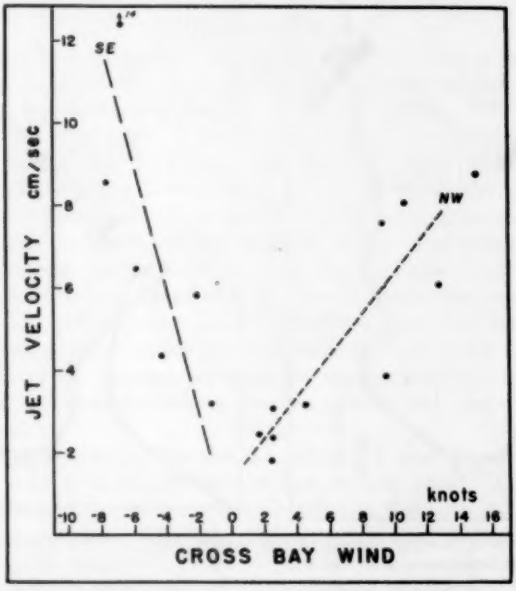


Fig. 4. Cross-bay wind component versus jet velocity relative to mean current. 1 meter depth. Wind as in figure 1.

able physical basis. Circulation patterns may repeat under similar wind conditions, and occasionally part of the pattern is present under practically any wind situation, e.g. the Picnic Point jet. Recognition and consideration of these patterns, even in a qualitative way, before taking plankton samples at one or several stations would prevent many of the "odd" or misleading results so often associated with this branch of limnology.

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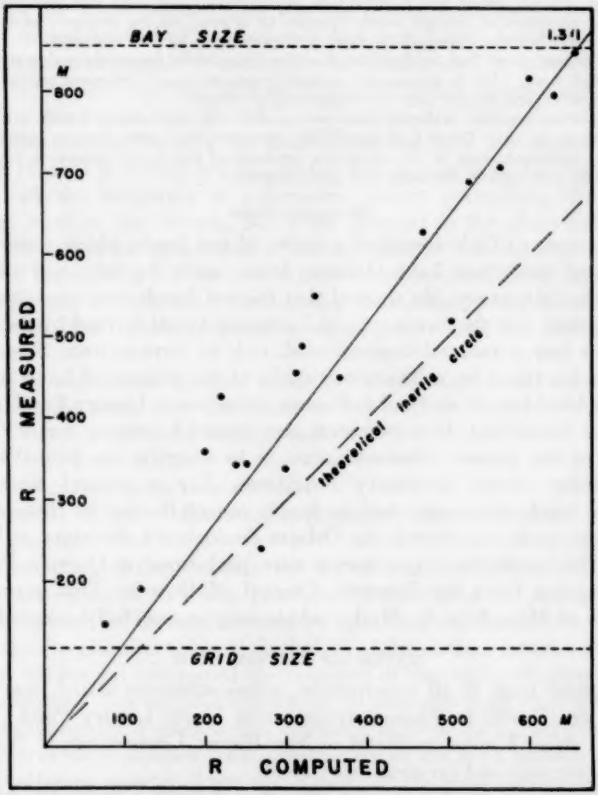


Fig. 5. Computed radius of inertia circle with velocity given by maximum outflow and inflow versus measured radius (i.e. half the distance between regions of maximum outflow and inflow).

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# A LABORATORY STUDY OF THE FORMATION OF SEDIMENT BANDS

J. R. VALLENTYNE

ABSTRACT. Reduced organic sediments from Lower Linsley Pond, Connecticut, develop a series of 12 to 15 red bands appearing successively from near the surface down to a depth of 6 millimeters. This occurs when the sediment is mixed with distilled water, flushed with nitrogen, and allowed to stand in test tubes in contact with air for about 150 days. The red bands are enriched in iron over the brown bands which separate them. Red bands are formed both in light and dark at room temperature but are not formed at 4°C. The bands do not form in a nitrogen atmosphere, nor do they form when toluene and phenol are added to the sediment. It is suggested that the red bands are typical Liesegang bands formed by the diffusion of oxygen into a reduced mud, rich in ferrous iron, with resulting periodic precipitation of ferric hydroxide. The process appears to depend on the presence of micro-organisms.

A series of three orange bands form successively upward from 6 mm beneath the sediment surface of a settled mixture of water and air-oxidized mud. The lowermost and first-formed orange band disappears after 25 days but is later replaced by other orange bands. The orange bands are enriched in acid-soluble iron over the intervening brown areas. The formation of orange bands appears to depend on the presence of micro-organisms. The lower parts of tubes of oxidized mud eventually become reduced.

Experiments show that oxidized mud settles completely from suspension more quickly than reduced mud. This is apparently caused by an increased sediment particle size, and perhaps an increased density also, accompanying oxidation.

There is no positive evidence that comparable red and orange bands are formed in lake sediments in situ. There is a possibility, however, that some ferrous sulfide bands of recent lake sediments may be the reduction products of red ferric hydroxide bands formed by Liesegang processes of diffusion and precipitation.

## INTRODUCTION

Sugawara (1934) described a series of red bands which were seen in a test tube of mud from Lake Haruna, Japan, after the tube had stood for a year in the laboratory. He showed that the red bands were enriched in iron and suggested that they were typical Liesegang bands formed by the diffusion of oxygen into a reduced organic mud, rich in ferrous iron. Sugawara did not prove his point by a laboratory study of the process of band formation. During a biochemical study of sediments from Lower Linsley Pond, Connecticut, it was found that these sediments also formed Liesegang bands. The main purpose of the present communication is to describe the formation of the bands under varied laboratory conditions. For a general discussion of Liesegang bands, the reader may profitably consult the text by Hedges (1932). Most of the work was done in the Osborn Zoological Laboratory of Yale University. The concluding experiments were performed at Queen's University, under a grant from the Research Council of Ontario. This permitted the assistance of Miss Alice G. Marks, whose help is gratefully acknowledged.

## MATERIALS AND METHODS

The mud used in all experiments, unless otherwise stated, was collected at 12 m depth with an Ekman dredge from Lower Linsley Pond. This lake is located about 4 miles northeast of New Haven, Connecticut, U. S. A. Fresh samples were collected for each experiment.

The widths of the bands were measured through a binocular microscope which had been removed from its base and attached horizontally to a retort stand. One eyepiece was fitted with a calibrated ocular micrometer. All test

tube experiments were carried out in tubes 25 by 150 mm. Measurements of each band were made at four roughly equidistant points around the circumference of the test tube. The point of first reading was selected at random, and the locations of the other three determined by that of the first. The four readings were averaged to give a measure of the widths of each band. Bands were not of uniform thickness throughout, and the average band width varied somewhat depending on the location of the points at which the readings were made. There was one case where a band was discontinuous, and two others where bands were slanted, but spiral bands (beginning at the band above and ending at the band below) were not observed in any of the experiments.

Although the microscopic arrangement permitted measurement of 0.03 mm, the bands were seldom sharply enough defined for this accuracy. Iron was determined colorimetrically with thiocyanate according to the method outlined in Hawk, Oser, and Summerson (1947).

## RESULTS

*Battery jar experiment.*—This was the initial experiment in which the formation of red ferric hydroxide bands was first noted. A battery jar, 4 × 7 cm in cross-section and 19 cm high, was filled with 170 ml of black mud from Lower Linsley Pond and 200 ml of distilled water (containing dissolved gases). The suspension was stirred until uniform and then allowed to settle at room temperature. Most of the mud settled out in a few minutes leaving the water colored a murky brown. At the end of one week the water began to clear with the formation of a flocculent brown precipitate. Most of the precipitate sank to the bottom, but some adhered to the glass walls. There was a slight indication of banding in the sediment at this time, but no formation of red bands. The jar was not critically re-examined for a month and a half. At the end of that time the banding was roughly the same as shown in figure 1A. The following zones were present (from the surface downwards):

1. A flocculent layer formed from the brown material which precipitated from the water after one week.
2. A yellow band at the mud surface.
3. A gray-brown band.
4. A zone containing two red bands.
5. A zone of gray sediment which graded into the reduced black mud beneath.

It was suspected that the color of the red bands was due to enrichment with ferric hydroxide, in which case one would expect the positions of the bands to depend on the diffusion of oxygen into the mud. An experiment was therefore performed to see if the height of the surface layers (all material above the red bands) influenced the positions of the red bands after the latter had been formed. The original battery jar of mud was used after it had stood in the laboratory for 5 months and appeared to show no further change. The surface layers were scraped from one-quarter of the mud surface and piled upon an adjacent quarter. Thus one-quarter of the mud surface was devoid of material above the red bands, another quarter had a double thickness of surface layers, and the remaining half was unchanged. The jar stood for

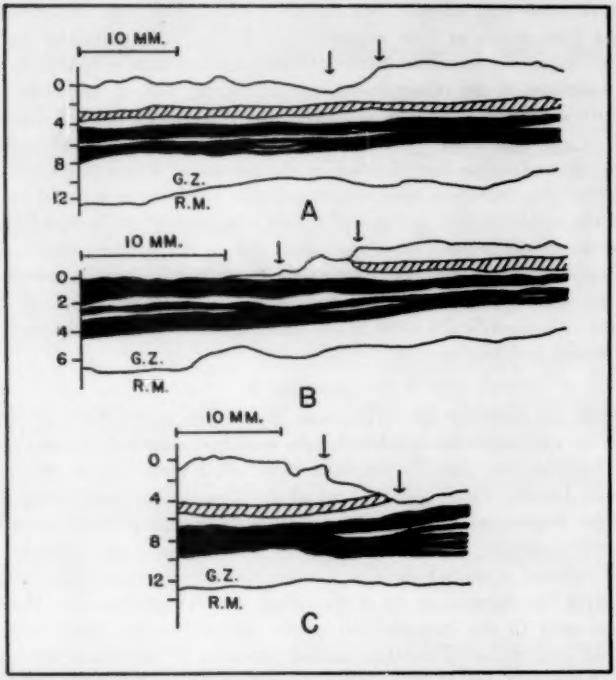


Fig. 1. The effect of modification of the surface layers on preformed red bands. See text. A, normal thickness of surface layers on left, double thickness on right; B, surface layers removed on left, normal thickness on right; C, double thickness of surface layers on left, surface layers removed on right. Yellow-brown band shown by diagonal lines; red bands shown in solid black; G. Z. gray zone; R. M. reduced mud. The vertical axis gives the distance in millimeters below the modified mud surface.

2½ months. At the end of that time the positions of the layers were traced on paper using a camera lucida arrangement. Figure 1 shows the appearance of the banding at the three junctions of interest. It is evident from figure 1 that the positions and widths of the red bands depend on the thickness of the surface layers, reaching the greatest extent when the surface layers are removed.

*Effect of the total depth of mud.*—Since the thickness of the surface layers influenced the positions of the red bands, it was questioned whether the total depth of mud had any effect. In the first experiment a series of test tubes were filled with varying amounts of a homogeneous mud-water mixture, and allowed to stand in the laboratory for one month. In all tubes the red bands appeared at about the same time and occupied approximately the same depths. A second experiment was performed using a series of four test tubes with paraffin slants in the bottom. The amount of reduced mud-water mixture added to each tube was adjusted in such a way that the mud surface was about 5 mm above the top of the paraffin slant. The zone where the red bands would form

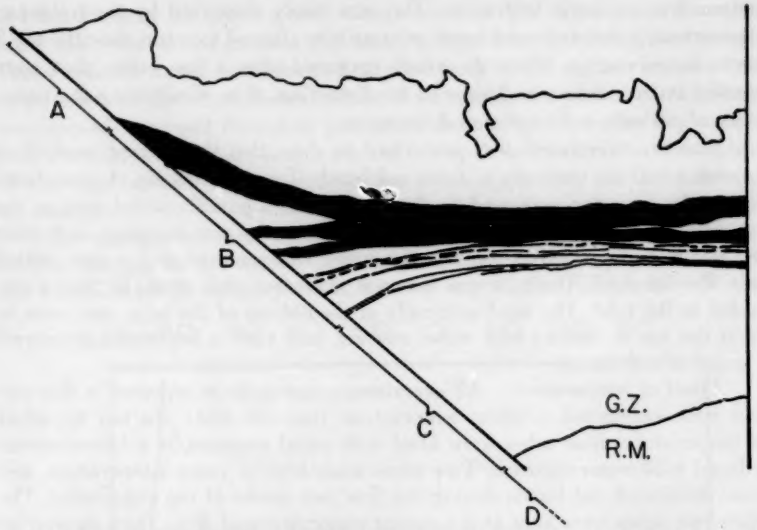


Fig. 2. Camera lucida tracing of banding in a battery jar of mud tilted 45° from the normal position. Only the left part of the jar is shown. A, B, C and D refer to surface layers, zone of red bands, gray zone and reduced mud, respectively. For explanation of other terms see figure 1.

was therefore entirely above the paraffin, yet the total depth of mud beneath varied from essentially 0 up to about 50 mm. None of the four tubes showed that the total depth of the mud influenced the positions of the red bands.

*Effect of glass walls.*—It was noted from the battery jar experiment that the depth of the red bands was greatest at the corners of the jar. In another experiment, a battery jar was filled with a reduced mud-water mixture and the mud allowed to settle with the jar tilted 45° from its normal position. In this way a triangular block of mud was formed, with the apex of the triangle at the bottom of the jar. The appearance of the red bands which developed is shown in figure 2. The fanning out of the red bands near the contact with the glass surface shows the pronounced effect which the glass wall may have. The results cannot be explained by the varying depth of mud, since the latter was found not to affect the positions of the red bands. Since all experiments reported in this paper were performed in glass containers it will be clear that the results are to some extent artificial, but the bands do extend throughout the mud. They are not just limited to the glass-mud interface.

An increased concentration of $O_2$ is to be expected wherever a glass wall prevents the 3-dimensional diffusion of a downward-moving diffusion front. The fanning of the red $Fe(OH)_3$ bands may thus be related to the diffusion of oxygen near the glass wall.

*Inversion of sediment.*—It could be argued that the formation of red bands resulted from a periodic type of sedimentation. In such a case, the diffusion of oxygen into the mud might merely reveal the bands by converting

ferrous iron to ferric hydroxide. This was easily disproved by the following experiment: a reduced mud-water mixture was allowed to settle, then the top 5 mm were mixed up. When the bands appeared after a few weeks, they were parallel to the surface and showed no distortion, thus eliminating the possibility of periodic sedimentation differences.

Another experiment was performed to show that the deepest mud (first to settle) had the capacity to form red bands if exposed to air. A glass tube, 25 mm in diameter, was used as the vessel, with a paraffin-sealed cork at the bottom. The tube was filled with a reduced mud-water mixture, and after red bands had formed at the top, the water was removed and a cork sealed over the top mud. The tube was inverted, the other cork removed, and water added to the tube. The mud originally at the bottom of the tube now came to lie at the top in contact with water and air, and after a few weeks developed a series of red bands.

*Effect of temperature.*—All experiments except those reported in this section were conducted at room temperature (uncontrolled). To test the effect of temperature, four tubes were filled with equal amounts of a homogeneous reduced mud-water mixture. Two tubes were kept at room temperature, and these developed red bands during the first two weeks of the experiment. The other two tubes were kept at a constant temperature of 4°C. They showed no sign of banding even after a period of 6 months. Low temperature is evidently unfavorable to band formation. The effect of temperature on red band formation merits more attention than we have given it.

*Effect of light.*—Light is known to be necessary for the formation of some types of Liesegang bands (Hedges, 1932). To test the influence of light, four tubes were filled with equal amounts of a homogeneous reduced mud-water mixture. Two tubes were kept in the dark and the other two under continuous light from a 60 watt bulb. No differences were noted between the light and dark tubes in the rate of band formation, the number of red bands or the positions of the red bands.

In all our experiments, tubes exposed to light developed a green color in the black reduced mud beneath the red bands. The green color was limited to the peripheral layer of mud (lacking in the central core). The development of the green color is completely inhibited by addition of bactericidal agents (phenol, toluene) to the mud. These facts suggest that the green color was due to the presence of green chemosynthetic bacteria which thrive in a reducing medium, yet require the presence of light for synthetic processes.

*Development of red bands in totally reduced mud.*—The development and appearance of red bands in tubes of reduced mud is quite variable unless all traces of oxygen are removed from the mud before the start of the experiment. In this experiment four test tubes were filled with equal amounts of a homogeneous reduced mud-water mixture. Nitrogen was bubbled through each of the tubes for 2 hours. Two tubes were tightly plugged with rubber stoppers and sealed with paraffin wax. The other two tubes were left exposed to air.

Of the two plugged tubes, one gave rise very slowly to a series of red bands, but it was later shown that this tube had developed a leak. Red bands

did not form in the other sealed tube even after 170 days, but a flocculent layer did form at the surface and three grayish-brown bands just beneath. These non-red bands corresponded to the bands in the surface layers of the open tubes, as described below. About 5 days after the perfectly sealed tube was opened, a second flocculent precipitate formed in the water. The conclusion from this experiment is that the red bands do not form in an atmosphere of nitrogen but that the non-red surface bands apparently can form in such an atmosphere.

The changes which occurred in one of the open tubes are shown in figure 3. The changes in the second open tube almost exactly duplicated those in the first. The events summarized in figure 3 may be described briefly. Within

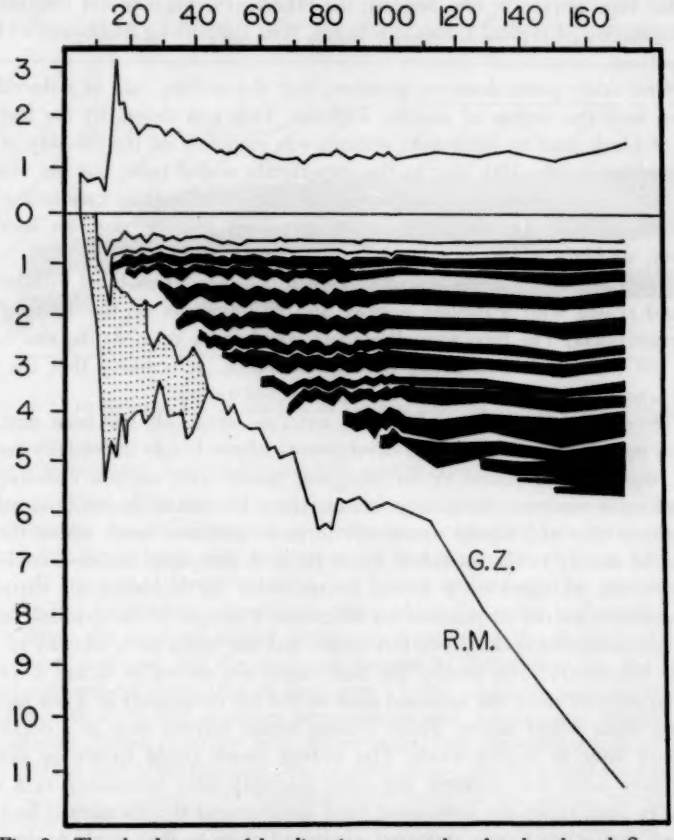


Fig. 3. The development of banding in a test tube of reduced mud. See text for explanation. The fine-grained black zone is shown stippled; the flocculent layer lies above the original mud surface; the three non-red bands are shown beneath the original mud surface. For explanation of other terms see figure 1. Vertical axis: distance in mm from original mud surface. Horizontal axis: time in days from start of experiment.

a few hours of the start of the experiment most of the black mud had settled out from the water; however some remained in suspension. On the 5th day part of the suspended matter precipitated from the water. This was augmented by a greater and more flocculent precipitate which appeared on the 16th day. A fine-grained black zone formed at the mud surface on the 5th day, the particles appearing smaller and blacker than those of the original black mud. This zone rapidly increased in depth until it was obliterated by a more slowly descending gray zone. A series of three non-red bands appeared beneath the original mud surface, and these were later followed by a series of red bands in the underlying mud. The gray zone was still descending at the end of the experiment. The results of this experiment show that red bands form in a fairly regular time sequence, one beneath the other, in a manner not dissimilar to the formation of typical Liesegang bands, thus supporting Sugawara's (1934) suggestion.

One other point deserves mention, that the settling rate of reduced mud varied with the degree of contact with air. This was shown by the last fraction of black mud to settle out: settling was complete on the 8th day in both open tubes, on the 10th day in the imperfectly sealed tube, but not until the 24th day in the perfectly sealed tube. The increased settling rate in the presence of air may be attributed to an increased particle size, an increased density, or both.

The tube whose development is shown in figure 3 was filled with mineral oil and sealed with a rubber stopper and paraffin wax on the 180th day of the experiment. The tube was allowed to stand for a year. At the end of that time the red bands had changed to black bands. It is likely that the black color was due to ferrous sulfide, but this was not tested.

*Development of orange bands in oxidized mud.*—It has been partly assumed up to this point that the development of red bands in initially reduced mud might be duplicated by an inorganic model with oxygen diffusing into a semi-solid medium containing ferrous iron. It seemed desirable to test the hypothesis that red bands would not form in oxidized mud, where the iron would be mostly in the immobile ferric form. A sample of reduced mud-water mixture was oxidized to a strong brown color by bubbling air through a mechanically stirred suspension for 48 hours. A sample of the oxidized suspension was added to each of two test tubes, and the tubes were allowed to stand in the laboratory. The results for both tubes are shown in figure 4. In contrast to reduced mud, the oxidized mud settled out completely in a few minutes, leaving clear water above. Thick orange bands formed first at a depth of 6 mm and later at higher levels. The orange bands could barely be detected when they were first formed, the color intensity later increasing to a maximum. In both tubes the lowermost band disappeared shortly after it had been formed, but other bands appeared afterward close to that level. A change in the surface mud in both tubes was noted about the 25th day. The surface layer assumed a spongy structure not unlike the flocculent layer of the reduced mud experiments.

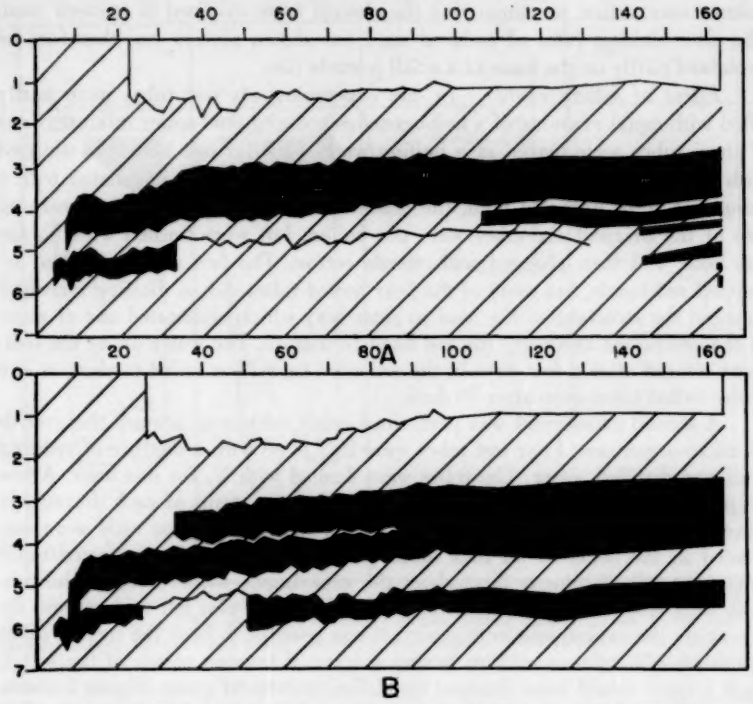


Fig. 4. The development of banding in two test tubes of oxidized mud. The spongy layer is shown as the clear area; brown mud by diagonal lines; orange bands by solid black. A, first test tube; B, second test tube. Vertical axis: distance in mm beneath mud surface. Horizontal axis: time in days from start of experiment.

Up until the 131st day the mud columns of both tubes remained uniformly brown (except for the spongy layer and orange bands), but between days 131 and 133 the column split into an upper brown and lower black half. The lower half contained irregular flecks of brown sediment. The junction between the two halves was exceedingly sharp. After the tubes had stood a total of 196 days, the mud in one of them was frozen and the upper and lower halves were analyzed for the ratio of ferrous to ferric iron by the rough method outlined by Pearsall and Mortimer (1939). Samples were thoroughly extracted with 1 N HCl at room temperature and the extracts filtered. The color density (after reaction with thiocyanate) was determined in a colorimeter before and after the addition of 30% $H_2O_2$. Several tests showed that the $Fe^{++}/Fe^{+++}$ ratio was approximately unity in the upper brown half, but 3.0-5.0 in the lower dark half. The darkening of the lower half was therefore due to a rather sudden increase in the amount of ferrous iron.

One other result should be mentioned. Concomitant with the formation of the reduced mud in the lower halves of the tubes there was a slight but significant decrease in the heights of the mud in the tubes. This suggests a

volume contraction accompanying the change from oxidized to reduced mud. The slow sinking rates of reduced mud (as shown above) can therefore be explained partly on the basis of a small particle size.

*Effect of killing agents.*—In one experiment six test tubes were partly filled with equal amounts of a homogeneous reduced mud-water mixture. Four of these tubes were placed in a boiling water bath for one hour and plugged with sterile cotton on removal. Two of the four tubes were inoculated with a sample of fresh unboiled mud, the other two left as controls. The remaining two of the original six tubes were not boiled, but were flushed with $N_2$ for one hour and then plugged with sterile cotton. The two unboiled tubes developed red bands, but none of the four boiled tubes did so. Boiling therefore changed the structure of the mud in some way which eliminated one or more of the conditions necessary for red band formation. The water above the sediment cleared after a few days in the unboiled tubes, but failed to clear in any of the boiled tubes even after 90 days.

A second experiment was performed using toluene to prevent the growth of micro-organisms. Four test tubes were half filled with a mixture of reduced mud and distilled water. The tubes were flushed with $N_2$ for one hour. A few drops of toluene were added to two tubes and the contents of each thoroughly mixed. The other two tubes were left as controls. Small glass vials were suspended in the necks of all four tubes. The vials in the toluene-treated tubes were kept full of toluene throughout the experiment, while those in the controls were filled with water. All four test tubes were plugged with cotton. By arranging the experiment in this way, it was possible to keep the treated tubes saturated with toluene without having a layer of toluene on top of the water. Such a layer would have changed the diffusion rates of gases. Figure 5 shows the sequence of changes which occurred in each of the tubes during the first few weeks of the experiment. The controls developed a series of red bands (only the zone of red bands is shown in figure 5) as was expected. The toluene-treated tubes did not develop red bands. The flocculent layer was much thicker in the treated tubes than in the controls. A gray zone formed in both treated tubes to a depth of 4 mm, and a second gray zone appeared in one tube (fig. 5D).

The results of the toluene experiment strongly suggest that the presence of micro-organisms is necessary for the formation of red bands. The critical experiment would have been to remove the toluene from treated mud to see if the mud still had the capacity to form red bands when inoculated with a sample of fresh mud. This experiment was not done. Other experiments were performed using 0.1% and 1.0% solutions of phenol, $HgCl_2$ and $PbCl_2$. Phenol prevented red band formation. The use of Hg and Pb salts gave variable results, red bands forming in some cases. Probably most of the Hg and Pb ions were precipitated as sulfides in the reduced mud. It is therefore tentatively concluded that micro-organisms are necessary for red band formation. On the other hand, the formation of the flocculent precipitate is apparently an inorganic process.

*Sediments from other lakes.*—Sediments were collected with an Ekman dredge from four other Connecticut lakes: East Twin Lake, Lake Quassapaug,

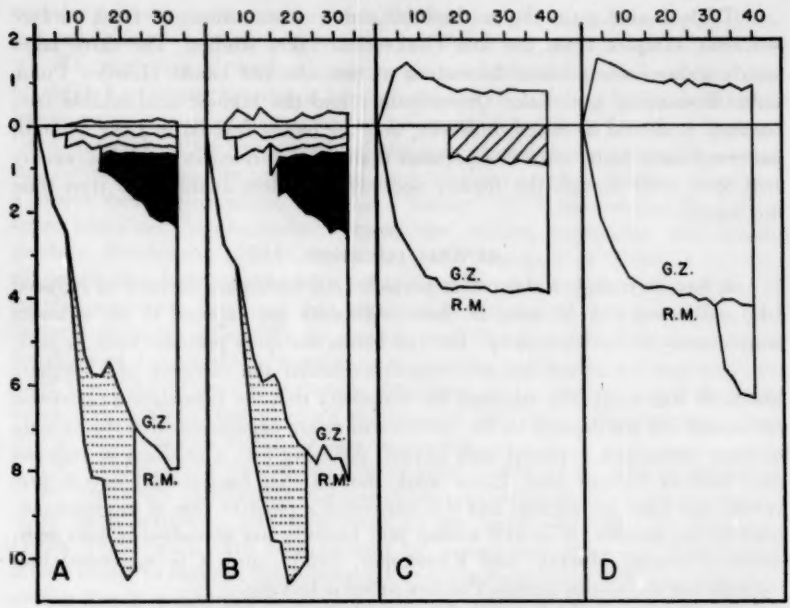


Fig. 5. Effect of toluene treatment on the development of banding in tubes of reduced mud. See text for explanation. A and B are control tubes; C and D are toluene-treated tubes. Zone of red bands shown in solid black. For explanation of other terms see figure 1. Vertical axis: distance in mm from original mud surface. Horizontal axis: time in days from start of experiment.

Lake Quonnipaug and Lake Waramaug. The reduced mud-water mixtures were allowed to settle in test tubes after $N_2$ flushing. Single red bands were formed in sediments from East Twin Lake and Lake Quassapaug, but there was no indication of truly periodic red bands. Periodic red bands were formed most markedly in the sediment from Lake Quonnipaug and somewhat less so in sediment from Lake Waramaug. The phenomenon is therefore not limited to sediment from Lower Linsley Pond, which was the source of the mud used in all other experiments.

*Iron analyses.*—In order to obtain samples from the various sediment layers for analysis, the supernatant water was poured off, and the mud frozen inside the test tubes. The banding was somewhat distorted by freezing. The samples analyzed are listed in table 1 together with the content of acid-soluble iron. The flocculent layer of the tubes of reduced mud was easily separated, but the uppermost two red bands and the interval between the second and third red bands were contaminated with adjacent material. The layers taken from the tube of oxidized mud were separated with little contamination. The results listed in table 1 show that both the red and orange bands were enriched in acid-soluble iron as compared to the intervening dark areas. Enrichment was most marked in the case of the orange bands analyzed.

Table 1 also gives the acid-soluble iron concentrations of fresh surface sediment samples from the five Connecticut lakes studied. The three lakes which showed unequivocal formation of periodic red bands (Linsley Pond, Lake Waramaug and Lake Quonnipaug) had the highest acid-soluble iron content. It should be noted, however, that the bands formed in Lake Quonnipaug sediment were more conspicuous than those formed in Lake Waramaug sediment, even though the former sediment had less acid-soluble iron than the latter.

## GENERAL DISCUSSION

It has been shown above that periodic red bands are formed in reduced lake sediments rich in iron, if those sediments are exposed to air at room temperature in the laboratory. The red bands are truly periodic both in position and time of formation, and thus come under the category of Liesegang bands. It was originally assumed for simplicity that the formation of periodic red bands did not depend on the presence of micro-organisms: that the process of band formation required only oxygen diffusing into a medium of reduced mud rich in ferrous iron. Later work showed that bactericidal agents prevented red band formation, and this suggested a positive role of micro-organisms in the process. It is well known that bacteria are abundant in lake sediments (Cooper, Murray, and Kleerkoper, 1953), and it is suggested that bacteria are the causal agents. Positive proof is lacking.

The question which concerns us is the manner in which the iron was precipitated. The oxidation-reduction potential of a ferrous-ferric system depends not only on the ratio of the two ions but also on the hydrogen ion activity. A precipitation of ferric iron may be caused either by a decrease in the hydrogen ion concentration or by an increase in the ratio of oxidizing to reducing substances in the environment. Under natural conditions in lakes the effective oxidizing agent is oxygen dissolved in the water (Mortimer, 1941, 1942). The lowering of oxidation-reduction potentials in lake waters and muds is mostly due to the utilization of dissolved oxygen in bacterial respiration (ZoBell, 1946). The sediment of Lower Linsley Pond is of the gyttja type, and it is apropos to note that Lönnerblad (1930) found that micro-organisms were especially active in gyttja. Lönnerblad studied the oxygen absorption of various sediments in test tubes. In one sample of untreated gyttja the oxygen was completely removed from the added water in 12 hours. A sterilized control contained oxygenated water even after 4 days. By analogy with lake sediments in situ and in vitro it is clear that bacteria must have been active in the sediments used for the study of red and orange band formation. The influence of bacteria could have been exerted by modifying the pH of the mud, the oxygen content, or the content of any number of compounds which undergo reversible oxidation-reduction. To cause the formation of periodic bands the bacteria would have to reach greatest abundance either in or out of phase with the red and orange bands. Both the red and orange bands have been examined for iron bacteria by Dr. R. J. Benoit (of the Philadelphia Academy of Natural Sciences) with negative findings. An extensive study of the role of bacteria in band formation is certainly warranted,

especially in conjunction with a detailed study of the microlayering of chemical conditions.

The structure of the ferric hydroxide precipitated from lakes at the time of the fall overturn has never been elucidated. Baudisch (1939) found that lepidocrocite was precipitated on oxidation of water from Saratoga Springs. Lord Rayleigh (1946) in a study of the iron of chalybeate waters found that two forms of iron were precipitated on oxidation: a yellow floating scum and a brown sunken precipitate. Hofer and Weller (1947) showed that the yellow scum contained lepidocrocite whereas the sunken precipitate was mostly goethite. Hutchinson (1944), by analogy with the work of Baudisch (1939), suggested that lepidocrocite was precipitated from lake water at the time of the fall overturn. Baudisch has performed experiments which suggest that bacteria respond differently to goethite and lepidocrocite. The question is therefore of fundamental importance in limnology. The flocculent precipitate from the reduced mud experiments described above was subjected to X-ray diffraction analysis, but gave no evidence of any known form of iron, even though chemical tests showed iron to be present.

The experiments on red and orange band formation all refer to sediments in the laboratory. Similar laminations in lake sediments in situ have apparently never been recorded, although some of the bands described by Perfiliew (1926, 1929) may have been formed by comparable processes. The failure of red bands to form in the laboratory at a temperature of 4°C. suggests that similar bands would not form in hypolimnic muds of lakes. The mud-water interface sampler used by Mortimer (1941, 1942) is capable of preserving sediment laminations. Neither Mortimer (personal communication) nor F. R. Hayes (personal communication) has found evidence of ferric hydroxide bands in any lakes studied with Mortimer's sampler. If the bands do form in lake sediments in situ, then there is of course the possibility that they may be confused with some types of varves.

TABLE 1

Iron Content of Lake Sediments and Test Tube Bands

The values refer to iron extractable with boiling 1N HCl in the presence of $H_2O_2$

| Sample | mg FeOOH per g dry wt. |
|---|---|
| Lower Linsley Pond | 55.6 |
| Lake Waramaug | 55.5 |
| Lake Quonnipaug | 33.4 |
| Lake Quassapaug | 22.7 |
| East Twin Lake | 16.2 |
| From a tube of initially reduced mud: | |
| Flocculent layer | 163.8 |
| Uppermost two red bands | 173.3 |
| Interval between 2nd and 3rd red bands | 48.0 |
| From a tube of initially oxidized mud: | |
| Just above uppermost orange band | 135.0 |
| Uppermost orange band | 537.4 |
| Just below uppermost orange band | 23.4 |

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